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DETAILED DESCRIPTION

[Detailed Description of the Invention]

They are the actuation approach and the manufacture approach of the electrode to an organic fuel cell list. The origin of background invention of invention Since invention stated on these specifications is invention made by the research done based on the contract with NASA, it must follow a convention of the general law 96-517 (35USC202) determined that contracting parties will hold a right.

Technical field This invention relates to a liquid supply mold organic fuel cell in detail about ** and an organic fuel cell generally.

Technique of a background A fuel cell is an electrochemical cell which free energy changes and is transformed into electrical energy by oxidation reaction of a fuel. In the case of organic / air fuel cell, an organic fuel like a methanol, formaldehyde, or a formic acid oxidizes with an anode, and becomes a carbon dioxide, on the other hand, it is returned with a cathode and air or oxygen becomes water. Since the specific energy of an organic fuel is high (for example, the specific energy of a methanol is 6232 Wh/kg), the fuel cell using an organic fuel is very attractive for both fixed application and some movable application.

The following two kinds are known as organic / an air fuel cell.

1. "an indirect type" or a "playback type (reforner)" fuel cell: The organic fuel becomes hydrogen which catalytic reaction regenerates and does not contain a carbon monoxide, and the hydrogen obtained by doing in this way oxidizes with the anode of a fuel cell.
2. -- "direct oxidation type" fuel cell: -- the organic fuel is directly supplied into a fuel cell, without being embellished chemically beforehand, and oxidizes with an anode.

A direct oxidation fuel cell has the unnecessary process which processes a fuel. Therefore, a direct oxidation fuel cell has whether an indirect fuel cell is endured in respect of weight and the volume, and the becoming advantage. The organic fuel supplied with a steam or a liquid is used for a direct oxidation fuel cell. The liquid supply structure of passing the anode of a fuel cell and generally circulating the liquid mixture of an organic fuel and a sulfuric-acid electrolyte is used for the promising direct oxidation fuel cell of a current technique.

Since the direct methanol fuel cell of a current technique uses the electrolyte of a sulfuric acid, it has many troubles. The ingredient which will use a sulfuric acid for manufacturing the fuel cell if a sulfuric acid is used, since corrosive is high is restrained remarkably. Generally, an expensive corrosion resistance ingredient is required. Since the sulfate ion generated in this fuel cell has the strong inclination to stick to an electrode catalyst, the reaction of a fuel of electric oxidation is checked and the engine performance of a fuel electrode falls. Moreover, a sulfuric acid tends to decompose at temperature higher than 80 degrees C, and the decomposition product contains sulfur and may usually make an electrode catalyst powerless. When a sulfuric-acid electrolyte is used in the case of a multi-cell stack, a parasitism short-circuit current (parasitic shunt current) may be produced.

The direct mold and indirect mold both typical fuel cell are indicated by U.S. Pat. No. 3,013,908, 3,113,049, 4,262,063, 4,407,905, 4,390,603, 4,612,261, 4,478,917, 4,537,840, 4,562,123, and 4,629,664.

For example, the liquid supply direct methanol fuel cell which uses the electrolyte of a sulfuric acid is indicated by U.S. Pat. No. 3,013,908 and 3,113,049. Amelioration of the sulfuric-acid base methanol fuel cell of decreasing that (crossover) which inserts the amount electrolyte of macromolecules or the solid-state proton conductivity film between an anode and a cathode as a layer (ionically conducting layer) which conducts ion, and an organic fuel moves to a cathode from an anode is indicated by U.S. Pat. No. 4,262,063, 4,390,603, 4,478,917, and 4,629,664. Although there is work which reduces migration when an ionic conduction layer is used, an ionic conduction layer is used only with a sulfuric-acid electrolyte. Therefore, this fuel cell has various kinds of above-mentioned faults which use a sulfuric acid as an electrolyte.

It is desirable to offer the liquid supply fuel cell which does not need a sulfuric acid as an electrolyte in view of the above-mentioned trouble accompanying using a sulfuric acid as an electrolyte.

In addition to amelioration of the operational characteristic of a liquid supply fuel cell, it is necessary to also improve the conventional manufacturing method of such a large surface area electrocatalysis electrode for fuel cells. The manufacturing method of **** of the electrode of a fuel cell requires time amount considerably, and is an expensive approach. If it states concretely, in order to manufacture an electrode, it is usually necessary to manufacture first the alloy powder supported by the carbon of large surface area by the chemical approach of requiring about 24 hours. If the alloy powder supported by carbon is manufactured, it will mix with a Teflon binder, and then, it applies to the base material of the carbon fiber base, and a gas diffusion electrode (gas diffusion electrode) is obtained.

In order to volatilize the impurity produced from a Teflon binder and to acquire the fiber matrix of Teflon, this electrode is heated up to 200 to 300 degree C. Among this heating step, oxidation and sintering of an electrode catalyst may take place and the activity of the front face of an electrode may fall. Therefore, after being activated again, it is necessary to use these electrodes in many cases. Moreover, the electrode manufactured with a conventional method is a gaseous diffusion mold, and since it is not suitably damp with liquid fuel, it cannot usually be effectively used for a liquid supply mold fuel cell.

Generally, the structure and the property of a fuel oxidation electrode (anode) which are used for a liquid supply mold fuel cell completely differ from the gas / a steamy supply fuel cell like hydrogen / oxygen fuel cell. The electrode structure used for a liquid supply fuel cell must be porosity very much, and a liquid fuel solution must wet all micropores. If the carbon dioxide generated with a fuel electrode is not effectively emitted from a reaction field, it does not have a rose. It is an important question to fully wet an electrode also for the fuel cell which uses the electrolyte of a sulfuric acid, although it is an important question for a liquid supply fuel cell.

It is desirable to offer the amelioration manufacture approach of the electrode used especially for a liquid supply fuel cell so that the above-mentioned thing may show. Moreover, it is desirable to also think out the approach of reforming it in order to use the electrode which fitted gas supply fuel cells for a liquid supply cell originally.

It is desirable to improve the liquid supply fuel cell itself, to offer and boil the amelioration manufacturing method of the electrode of a fuel cell, in addition to offer an effective new fuel. It is desirable to offer the liquid fuel with which perfect and efficient electrochemistry oxidation is generally made within a fuel cell.

Effective use of the organic fuel within a direct oxidation fuel cell is influenced by the ease at the time of generally the organic compound oxidizing with the anode in a fuel cell. A conventional organic fuel like a methanol is quite difficult for carrying out electric oxidation. Especially electric oxidation of an organic compound like a methanol is a process (very hindered process) which a multiplex electronic transition (multiple electron transfer) is performed, and has many middle steps and which was restricted very much. A dissociative adsorption is carried out and the activity surface kind with which a fuel molecule oxidizes comparatively easily at these steps It accomplishes. The ease of electric oxidation is usually determined by that a dissociative adsorption and surface reaction are easy. Although the formaldehyde of the conventional fuel the outside of it oxidizes still more easily, it has other faults. For example, toxicity is very strong. Moreover, since it is very easy to dissolve formaldehyde in water and

moves to the direction of the cathode of a fuel cell, the engine performance of a fuel cell falls. The conventional organic fuel the outside of it, for example, a formic acid, is corrosive. Furthermore, during electric oxidation, since many of conventional organic fuels spoil the electrode of a fuel cell, it bars prolonged actuation. It is desirable to offer the amelioration fuel which conquers the fault of a conventional organic fuel like a methanol, formaldehyde, and a formic acid and which is used especially for a liquid supply fuel cell so that clearly from the above-mentioned thing.

Outline of invention The general purpose of this invention is offering the improved direct mold liquid supply fuel cell. A special one division target of this invention is offering the direct mold liquid supply fuel cell which does not need the electrolyte of a sulfuric acid. Other special purposes of this invention are fully wetting the electrode used for a liquid supply fuel cell. The purpose of further others of this invention is offering the amelioration approach of wetting the electrode used with the fuel cell which has a sulfuric-acid electrolyte. Other special purposes of this invention are offering the improved fuel which is used for a liquid supply fuel cell further.

The purpose which offers the improved liquid supply direct fuel cell which does not need a sulfuric-acid electrolyte is attained in part by using a solid-state polymer electrolyte membrane in the cell mold anode and combination which are porosity and can be soaked in a fuel. By the amelioration liquid fuel cell, the cell mold anode structure and a cathode are combined with both sides of the solid-state polymer proton conductivity film, and a film-electrode assembly object is formed. The anode side of this assembly is passed and the solution of the methanol which does not contain a sulfuric acid substantially, and water is circulated.

The solid-state polymer film is excellent in electrochemical stability and mechanical stability, since ion conductivity is high, it is used partially, and it can function as both electrolyte and separator. Moreover, compared with the interface of an electrode/sulfuric acid, the interface of an electrode / film electrolyte is easier for the reaction of electric oxidation and air of a methanol, or oxygen of electric reduction. If this film is used, a fuel cell can be operated at 120 degrees C and high temperature. Since the solution of a fuel and water does not contain the sulfuric acid substantially, the corrosion resistance member expensive for a fuel cell and its accessory is unnecessary. It exists, when the sulfuric-acid electrolyte is used. Since the conductive ion in the solution of a fuel and water does not exist, possibility that a parasitism shunt current will arise in a multi-cell stack disappears substantially.

As the above-mentioned solid-state polymer electrolyte, film:Nafion (trademark) of proton conductivity cation exchange membrane, for example, a perfluoro-^{**} sulfonic-acid polymer, is desirable. Nafion is the copolymer of tetrafluoroethylene and a perfluoro-vinyl ether sulfonic acid. The film of the complex of a reforming perfluoro-^{**} sulfonic-acid polymer, the Pori hydrocarbon sulfonic acid, and two or more sorts of proton exchange film can also be used.

As for an anode, it is desirable to manufacture by the particle of the large surface area of the platinum base alloy of noble metals and non-noble metals. It can perform using the constituent of two components and three components for performing electric oxidation of an organic fuel. The platinum-ruthenium alloy which has the presentation to which platinum was changed in the range of ten to 90 atomic percent is the electrode catalyst of an anode desirable although electric oxidation of the methanol is carried out. this alloy particle -- the gestalt of detailed metal powder, i.e., the gestalt "which is not supported", -- and -- or it is the gestalt supported by the carbon material of large surface area.

The conventional fuel cell anode structure (gaseous diffusion mold) is not suitable for using it for liquid supply mold organic / air fuel cell. The electrode of these former is damp to a fuel, and its property is low. The electrode of these former can be reformed to liquid supply mold fuel cells by carrying out a coat by the matter which is damp and improves a property. Although Nafion which has the 1000 or more equivalents is the desirable matter, this additive reduces the boundary tension of a liquid / catalyst interface, the pore and the particle of an electrode come to get wet in homogeneity with the solution of a fuel and water, and use of an electrode catalyst is promoted. It gets wet and a property is improved, and also the Nafion additive can give an ion continuity (ionic continuity) to a solid-electrolyte membrane, and can move effectively the proton or hydronium ion generated in fuel oxidation reaction by fuel oxidation reaction. Furthermore, balking of the pore of an electrode to a carbon dioxide becomes easy

with this additive. By using a perfluoro-****** sulfonic acid as an additive, an anion radical is strong to the interface of an electrode/electrolyte, and it does not adsorb. As a result, electric oxidation reaction of a methanol becomes easier than the case of a sulfuric-acid electrolyte. As other hydrophilic proton conductivity additives which have a desirable property, there are the mixture and the phosphate water ****** zirconium of montmorillonite clay, alkoxy celluloses, cyclodextrin, and zeolites.

The purpose which improves the electrode which operates within a liquid supply fuel cell is partially attained by using a perfluoro-octane sulfonic acid as an additive into the electro-deposition bath used for manufacturing an electrode. It consists of steps which impress an electrical potential difference between this anode and a cathode until the electrodeposition process which uses a perfluoro-octane sulfonic acid as an additive arranges the carbon-electrode structure of large surface area in a metal salt content bath, and arranges an anode in this bath and then the metal of the amount of requests electrodeposits it in an electrode. After making an electrode electrodeposit a metal, an electrode is taken out from a bath and it washes within deionized water.

As a desirable metal salt, there are a hexachloroplatinic acid and a potassium pen TAKUROOAKO ruthenium. The anode consists of platinum. There is a carbon particle of the large surface area combined as the carbon-electrode structure by the polytetrafluoroethylene currently sold of trademark Teflon (trademark).

The purpose which fully wets an electrode within the liquid supply fuel cell which has a sulfuric-acid electrolyte is attained by using a perfluoro-octane sulfonic acid for the fuel mixture of a fuel cell as an additive. As for a perfluoro-octane sulfonic acid, it is desirable to add into the mixture of an organic fuel and water by the concentration of 0.001-0.1M.

The general purpose which offers the new fuel used for an organic fuel cell is attained by using trimethoxy methane, dimethoxymethane, or a trioxane.

Within a fuel cell, without spoiling an electrode, all of these three sorts of new fuels can be high-speed, they can oxidize, and can become a carbon dioxide and water. Furthermore, neither trimethoxy methane nor dimethoxymethane nor a trioxane is corrosive. The oxidation rates of these three sorts of new fuels are the conventional organic fuel and more than an EQC. For example, the oxidation rate of dimethoxymethane is higher than a methanol at the same temperature. The trioxane has attained the oxidation rate equivalent to formaldehyde. However, since molecular weight is farther [than formaldehyde] high, a trioxane does not move to the direction of the cathode of a fuel cell easily like the molecule of formaldehyde.

Trimethoxy methane, dimethoxymethane, and a trioxane can be used for the fuel cell which has either of the above-mentioned improving points. However, these amelioration fuel can be used in favor of other organic fuel cells including the conventional whole fuel cell.

Based on these things, the various general purposes of above-mentioned this invention are attained. Other purposes and advantages of this invention will become clear by explanation of the following details.

easy explanation of a drawing the purpose and advantage of this invention are still more easily clear, if the above detailed explanation and detailed accompanying drawing are referred to -- what -- I will come out.

Drawing 1 is a mimetic diagram of an amelioration liquid supply organic fuel cell which was constituted according to the desirable embodiment of this invention and which has the solid-state polymer film.

Drawing 2 is the mimetic diagram of the multi-cell fuel system using the amelioration liquid supply organic fuel cell shown in drawing 1.

Drawing 3 is a graph which shows the engine performance of the solid-state polymer film electrolyte in the inside of a liquid organic fuel, and a sulfuric-acid electrolyte.

Drawing 4 is a graph which shows the engine performance of the liquid supply fuel cell shown in drawing 1 of the combination case of a methanol / air, and a methanol/oxygen.

Drawing 5 is a graph which shows the effectiveness of the concentration of a fuel over the engine performance of the liquid supply fuel cell shown in drawing 1.

Drawing 6 is a graph which shows the polarization behavior of the fuel electrode of a fuel cell, and a

cathode shown in drawing 1.

Drawing 7 is a block diagram which is used for a fluid supply cell and in which showing the manufacturing method of the electrode containing the proton conductivity ionomer additive of a hydrophilic property.

Drawing 8 is a graph which shows the polarization property of the methanol oxidation in the electrode manufactured according to the approach which contains an ionomer additive and is shown in drawing 7.

Drawing 9 is a block diagram which uses a perfluoro-octane sulfonic acid in an electro-deposition bath and in which showing the manufacture approach of an electrode.

Drawing 10 is the mimetic diagram of the electrochemical cell used in case the approach shown in drawing 9 is enforced.

Drawing 11 is an instantiation polarization curve in the case of manufacturing an electrode using the approach of drawing 9.

Drawing 12 is a graph which illustrates the polarization curve of a fuel cell which uses a perfluoro-octane sulfonic acid as fuel additive, using a sulfuric-acid electrolyte.

Drawing 13 is a graph which illustrates the polarization curve of a fuel cell which uses dimethoxymethane as a fuel on various fuel concentration level into the half cell which has a sulfuric-acid electrolyte.

Drawing 14 is a graph which changes the temperature and concentration in the half cell which has a sulfuric-acid electrolyte, and illustrates the polarization curve of the fuel cell using dimethoxymethane as a fuel.

Drawing 15 is a graph which shows the cell voltage as a function of current density of the fuel cell of drawing 1 which uses dimethoxymethane as a fuel.

Drawing 16 is a graph which illustrates the polarization curve of the fuel cell which uses trimethoxy methane as a fuel on various fuel concentration level in the half cell which has a sulfuric-acid electrolyte.

Drawing 17 is a graph which changes the temperature and concentration in the half cell which has a sulfuric-acid electrolyte, and illustrates the polarization curve of the fuel cell using trimethoxy methane as a fuel.

Drawing 18 is a graph which shows the cell voltage as a function of current density of the fuel cell of drawing 1 which uses trimethoxy methane or a methanol as a fuel.

Drawing 19 is a graph which illustrates the polarization curve of the fuel cell which uses trimethoxy methane as a fuel on seed fuel concentration level in the half cell which has a two-mol sulfuric-acid electrolyte.

Drawing 20 is a graph which illustrates the polarization curve of the fuel cell which changes the temperature and concentration of a sulfuric-acid electrolyte in a half cell, and uses trimethoxy methane as a fuel.

Drawing 21 is a graph which illustrates the cell voltage as a function of current density of the fuel cell of drawing 1 which uses trimethoxy methane as a fuel.

Detailed description With reference to many drawings, the desirable embodiment of this invention is explained below. The amelioration liquid supply organic fuel cell which uses an individual polymer electrolyte membrane and the anode additive of an ionomer first is mainly described with reference to drawing 1 -6. Next, about the manufacturing method of the anode which has an ionomer additive, drawing 7 -8 are made reference and they are described. How to get wet by manufacturing an electrode within the bath containing a perfluoro-octane sulfonic acid, and to improve a property is described with reference to drawing 9 -11. About the fuel cell which uses a perfluoro-octane sulfonic acid as fuel additive, drawing 12 is made reference and explained. Dimethoxymethane, trimethoxy methane, and a trioxane are explained with reference to drawing 13 -21 about the fuel cell used as a fuel.

Fuel cell using an individual proton conductivity electrolyte membrane Drawing 1 shows the liquid supply organic fuel cell 10 equipped with housing 12, the anode 14, the cathode 16, and the individual polymer proton conductivity cation exchange electrolyte membrane 18. The single multiplex layer

composite-construction object of an anode 14, a cathode 16, and the individual polymer electrolyte membrane 18 is desirable, and they carry out the film 1 electrode assembly name of this on these specifications so that it may explain further below at a detail. The pump 20 is installed in order to carry out pumping of the solution of an organic fuel and water into the anode room 22 of housing 12. The mixture of the organic fuel and water is taken out from an exit port 23, and recycling is carried out through the recycling system which has the methanol tank 19 and which is explained below with reference to drawing 2. The carbon dioxide generated at the anode room is emitted through the port 24 in a tank 19.

The compressor 26 of oxygen or air is formed in order to supply oxygen or air all over the cathode room 28 in housing 12. Drawing 2 explained below shows the fuel cell system incorporating the staff of each fuel cell who has a recycling system. The following detailed explanation of the fuel cell of drawing 1 mainly performs the structure and the function of an anode 14, a cathode 16, and the film 18 as a core. Before using it, the anode room 22 is filled with the mixture of an organic fuel and water, and fills the cathode room 28 with air and oxygen. An organic fuel passes and circulates through an anode 14 during actuation, on the other hand, pumping of oxygen or the air is carried out into the cathode room 28, and it passes and circulates through a cathode 16. If it connects with the electric load (not shown) anode 14 between cathodes 16, electric oxidation of an organic fuel will take place with an anode 14, and electric reduction of oxygen will take place with a cathode 16. If a reaction which is different with an anode and a cathode occurs, an electrical-potential-difference difference will arise in these 2 inter-electrode. The electron generated by electric oxidation with an anode 14 conducts through an external load (not shown), and, finally is caught with a cathode 16. The hydrogen ion and proton which were generated with the anode 14 cross the film electrolyte 18, and are directly conveyed toward a cathode 16. Therefore, a current is held with the electron which passes the flow and the external load of the ion which passes a cell.

As mentioned above, an anode 14, a cathode 16, and the film 18 form the layer structure object of single complex. In the desirable embodiment, the film 18 is manufactured by Nafion (trademark) of a perfluoro-****** proton exchange film ingredient. Although Nafion (trademark) is the copolymer of tetrafluoroethylene and a perfluoro-vinyl ether sulfonic acid, it can use other film ingredients. For example, the film of the complex of a reforming perfluoro-****** sulfonic-acid polymer, the Pori hydrocarbon sulfonic acid, and two or more sorts of proton exchange film can be used. an anode 14 is manufactured by the particle of a platinum-ruthenium alloy -- having -- these particles -- as the end of a detailed metal grain (i.e., "not supported") -- or it distributing on the carbon of large surface area, namely, "it being supported." The carbon of large surface area is U.S. Cabot. Vulcan which an Inc. company offers An ingredient like XC-72A is sufficient. The backing (not shown) of a carbon fiber sheet is used in order to perform the particle and electrical connection of the electrocatalysis. A commercial Toray (trademark) paper is used as an electrode backing sheet. The alloy electrocatalysis supported by the backing of a Toray (trademark) paper can obtain from E-Tek of the U.S. Massachusetts hula MINGAMU whereabouts, and an Inc. company. Or it can join together with Teflon binding material, and the electrocatalysis which is not supported and the supported electrocatalysis can be manufactured by the chemical approach of applying on Toray paper backing and manufacturing an anode. How to manufacture an electrocatalysis electrode, without spending many hours efficiently is explained below at a detail.

The alloy of the platinum base whose second metal is tin, iridium, an osmium, or a rhenium can be used instead of a platinum-ruthenium. Generally, an alloy is chosen in relation to the fuel used for a fuel cell. It is desirable although a platinum-ruthenium carries out electric oxidation of the methanol. In the case of a platinum-ruthenium, the amount added in an electrocatalysis layer is 0. The range of 2 is desirable cm 5-4.0mg /. Electric oxidation with the much more efficient higher one is realized rather than addition level is low.

A cathode 16 is a gas diffusion electrode and a platinum particle is joint ***** to one field of the film 18. or [by which the cathode 16 was combined with the field of the opposite side of the anode 14 of the film 18 / not being supported] -- or manufacturing with the platinum currently supported is

desirable. U.S. Johnson Matthey The supported platinum ingredient which can come to hand from the platinum black (fuel cell grade) which can come to hand from an Inc. company, and which is not supported or U.S. E-Tek, and an Inc. company fits cathodes. In the case of an anode, it is desirable to carry the metal particles for cathodes on a carbonaceous backing ingredient. The amount which carries out the load of the electrocatalysis particle on carbon backing has the desirable range of 0.5 - 4.0 mg/cm². Hydrophobicity required to remove efficiently the water which the backing of an electrocatalysis alloy and a carbon fiber contained 10 - 50% of the weight of Teflon, and generated the three-phase zone, and was generated by electric reduction of oxygen is offered.

During actuation, a density range passes the anode 14 in the anode room 22, and circulates the fuel of 0.5-3.0 mols / L, and the mixture (the acid or alkaline electrolyte is not contained) of water. The rate of flow to be used has the desirable range of 10 - 500 mL/min. When the mixture of a fuel and water passes and circulates through an anode 14, in the case of a typical methanol cell, the following electrochemical reaction occurs and an electron is emitted.

Anode: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ (1)

The carbon dioxide generated at the above-mentioned reaction is taken out through an outlet 23 with the solution of a fuel and water, and is separated from this solution by the vapor-liquid-separation machine (with reference to drawing 2, it explains below). Next, recycling of the solution of a fuel and water is carried out into a cell with a pump 20.

The electrochemical reaction shown with the above-mentioned equation (1) and other electrochemical reaction which performs electric reduction of oxygen which catches an electron to coincidence occur in a cathode 16, and is expressed by the following equation.

Cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2\text{O}$ (2)

The general reaction of the typical methanol fuel cell expressed with the following equation is performed by each electrode reaction indicated to be an equation (1) by (2).

Cell: $\text{CH}_3\text{OH} + 1.5\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ (3)

Current density higher than 500 mA/cm² is maintainable with the fuel of concentration high enough. However, by such concentration, the passing speed of the fuel which crosses the film 18 and faces to a cathode 16 increases even to extent to which the effectiveness and the electrical order of the fuel cell fall remarkably. By concentration lower than 0.5 mol/L, actuation of a cell is limited to less than two 100 mA/cm current density. It was found out that the low rate of flow can apply in the case of low current density. Since the matter transportation rate to the anode of an organic fuel is increased in order to remove the carbon dioxide generated according to electrochemical reaction when making it operate with high current density, the high rate of flow is required. Moreover, by the low rate of flow, the film of a fuel is passed and the migration to a cathode from an anode decreases.

As for oxygen or air, it is desirable to pass and circulate a cathode 16 under the pressure of the range of 10 - 30psig. In the case of high current density, with a pressure higher than the external pressure force, the mass transport of the oxygen to the part of electrochemical reaction is improved especially. The water generated by electrochemical reaction in a cathode is transported from the cathode room 28 by the flow of oxygen through a port 30.

In addition to electric oxidation being carried out with an anode, the liquid fuel which is dissolving in water penetrates the solid-state polymer electrolyte membrane 18, and combines it with the oxygen of the front face of the electrocatalysis of a cathode.

This process mentions a methanol as an example and is shown in the equation (3). This phenomenon is called "fuel migration (fuel crossover)." A fuel is consumed without the action potential of an oxygen electrode falling and generating useful electrical energy by migration of a fuel. Generally, migration of a fuel is a parasitism reaction which effectiveness is reduced, and the engine performance is reduced and generates heat within a fuel cell. Therefore, it is desirable to make passing speed of a fuel into min. This passing speed is proportional to the permeability of the fuel which passes a solid-electrolyte membrane, concentration increases, and it increases as temperature rises. The permeability over membranous liquid fuel can be reduced by choosing a solid-electrolyte membrane with low moisture content. If the permeability over a fuel is reduced, passing speed will fall. Moreover, the fuel with a large molecular

size has a diffusion coefficient smaller than a fuel with a small molecular size. Therefore, permeability can be lowered by choosing a fuel with a large molecular size. Although a water-soluble fuel is desirable, the fuel of a medium shows permeability with low solubility. Since the fuel of a high-boiling point does not evaporate, transportation which leads the film of such a fuel is performed by the liquid phase. Since steamy permeability is higher than a liquid, generally the fuel of a high-boiling point has low passing speed. Moreover, the concentration of liquid fuel may be lowered in order to lower passing speed. The hydrophobic section and the anode structure over which the hydrophilic part is distributed the optimal prevent that fully get wet with liquid fuel, and electrochemical reaction is fully held, and the fuel of an excessive amount approaches a film electrolyte. Therefore, if the anode structure is chosen suitably, high performance and desirable low passing speed can be obtained.

Since a solid-electrolyte membrane can penetrate water at temperature higher than 60 degrees C, most quantity of water crosses the film and is conveyed by transparency and evaporation. The water conveyed through a solid-electrolyte membrane is condensed within a water recovery system, and then is sent to a water tank (this system and tank are explained below with reference to [drawing 2](#) at a detail), and recycling of that water can be carried out all over the anode room 22.

Inter-electrode [two] is conveyed to the water generated with the proton generated with the anode 14, and the cathode 16 by the proton conductivity solid-electrolyte membrane 18. It is important for operating organic / air fuel cell effectively to maintain the high proton conductivity of the film 18. The moisture content of an electrolyte membrane is maintained by making it contact liquid fuel, the mixture of water, and directly. In order that the thickness of a proton conductivity solid-state polymer electrolyte membrane may make a dimension stability, the range of it must be 0.05-0.5mm. Although the film thinner than 0.05mm brings about the membrane electrode assembly object in which opportunity reinforcement was inferior, on the other hand, with liquid fuel, it swells, and the polymer is going too far, and, as for the film thicker than 0.5mm, shows a lifting and superfluous resistance for change of the dimension which does damage. The ion conductivity of an electrolyte membrane must be larger than $10\text{hm}^{-1}\text{cm}^{-1}$, in order to hold the internal resistance which can permit a fuel cell.

As mentioned above, the permeability of an electrolyte membrane over liquid fuel must be low. The film of a perfluoro-²² sulfonic-acid polymer like Aciplex (trademark) (Japan's Asahi Glass Co. company manufacture) to which Nafion and a property are similar although it was found out that the Nafion film is effective as a proton conductivity solid-state polymer electrolyte membrane, and U.S. Dow Chemical The polymer film 13204.10, for example, XUS, which Co. company is manufacturing can be used. The film of polyethylene and a polypropylene sulfonic acid, the film of polystyrene sulfonate, and the film (for example, film which U.S. RAI Corporation manufactured) of other Pori hydrocarbon base sulfonic acids can also be used by the temperature and the period when a fuel cell operates. Low fuel permeability can be attained using the film of the complex which consists of two or more sorts of proton conductivity cation exchange polymers from which the acid equivalent differs, the chemistry organization differs, water content differs, or the class and extent of bridge formation differ (for example, the bridge is constructed by multivalent cations, such as aluminum³⁺ and Mg²⁺). ²² -- the film of complex [like] can be manufactured and high ion conductivity, the low permeability over liquid fuel, and the outstanding electrochemical stability can be attained.

By using the solid-state poly membrane of proton conductivity as an electrolyte, the electrolyte of a free fusibility acid or a base is unnecessary, and a liquid supply direct oxidation type organic fuel cell is obtained so that I may be understood from the above explanation. The only electrolyte is the solid-state poly membrane of proton conductivity. The acid of a free gestalt does not exist in the mixture of liquid fuel and water. Since a free acid does not exist, the corrosion by acid induction of the cell components which tend to happen in the organic substance / air fuel cell of the acid base of a working technique is avoided. This brings considerable flexibility to the ingredient selection for a fuel cell and a coordinated subsystem. Furthermore, since the carbonate of fusibility is not formed unlike the fuel cell which contains a potassium hydroxide as a liquid electrolyte, the cell engine performance does not fall. Moreover, a parasitism short-circuit current is avoided by use of a solid-electrolyte membrane. Subsequently, with reference to [drawing 2](#), the fuel cell system which adopted what made the stack fuel

cell plurality similar to the fuel cell shown in drawing 1 is explained. This fuel cell system contains the stack 25 of a fuel cell, and has the film / electrode assembly which each explained above with reference to drawing 1. Oxygen or air is supplied by the oxidizer feeder 26. This may be for example, an oxygen supply bomb, an air blower fan, or an air compressor. The mixture of air and water or the mixture of oxygen and water is sampled through an exit port 30 from a stack 25, and is carried to the water recovery system 27. The water recovery system 27 operates so that air or oxygen may be separated from water.

A part of air separated by equipment 27 or oxygen is returned to the oxidizer feeder 26, and it is again put into a stack 25. A fresh air or oxygen is added to a feeder 26. The water separated by equipment 27 is supplied to a fuel and the water injector 29, and, similarly organic fuels, such as a methanol, are supplied there from the storage tank 33. An injector 29 mixes the water from a recovery system 27 with the organic fuel from a tank 33, and produces the water/fuel solution which the fuel dissolved into water.

The fuel/water solution made by the injector 29 are supplied into the circulation tank 35. The fuel / water mixture containing a carbon dioxide are sampled from a stack 25 through a port 23, and is supplied into a circulation tank through the heat exchange machine 37. Therefore, the circulation tank 35 receives both the solution of the fuel/water from an injector 29, and the fuel/water solution of the carbon-dioxide-gas content from the heat exchange machine 37. The circulation tank 35 extracts a carbon dioxide from a fuel / water mixture, and emits a carbon dioxide through a bleeder 39. The solution of the fuel/water which remained as a result is supplied into a stack 25 through a pump 20. The circulation tank 35 can be located between a stack 25 and the heat exchange machine 37, can remove a carbon dioxide in front of a heat exchange machine, and can also raise work of a heat exchange machine.

Actuation of the various element parts illustrated by drawing 2 is explained in more detail below. The circulation tank 35 is a column which has large top space. The fuel / water mixture of the liquid which received from the injector 29 are added into the top of the column. The fuel / water mixture which has a carbon dioxide in inside are supplied into the bottom part of a column. The choke damp wide opened from a fuel / water mixture is accumulated in the top space, and, finally is discharged. the fuel / water mixture which replaces and contains a carbon dioxide are like Celgard (trademark) or GOATEKKUSU (trademark) -- fine -- letting the inside of the bundle of hole ingredient tubing pass -- a fine hole -- liquid fuel can flow in accordance with the shaft of tubing, making gas emit through the wall of tubing of an ingredient. Celgard [Celgard] (trademark) and GOATEKKUSU [GoreTex] (trademark) are U.S. Celanese. Corp. and Gore It is the trademark of Association.

In order to separate a carbon dioxide from a fuel / water mixture, the need of forming an external circulation tank using a static recycling system (not shown) into the anode chamber of a stack 25 can also be abolished. In such a system, the bubble of a carbon dioxide tends to go up the inside of an anode chamber perpendicularly for a buoyancy by birth. By the viscous interaction with the liquid fuel mixture which encloses air bubbles, liquid fuel is taken upward with it in the direction of an exit port 23. Once it comes out of an anode chamber outside, a liquid opens gas wide, will carry out a perimeter and heat exchange, and will get cold, and concentration will become high rather than the liquid in a cell. The liquid with more high concentration is supplied through an inlet-port port into the pars basilaris ossis occipitalis of an anode chamber. Instead of spending electrical energy on a pump, a static recycling system uses well the heat and gas which occur within a cell. Although the above-mentioned process forms radical Motohara ** of a static recycling system, it is not explained to a detail any more here. If a static recycling system is used, the orientation to which a fuel cell can operate will be restricted and it may be able to perform only to static application.

Test result for the fuel cell which has the Nafion (trademark) electrolyte membrane The behavior of electric oxidation of the methanol to a sulfuric-acid electrolyte and the Nafion (trademark) electrolyte has been studied by the electrostatic ***** measuring method (galvanostatic polarization measurements) in an electrochemical cell (what was similar to the electrodeposited cell shown below at drawing 10 although not illustrated). The cell consists of the working electrode, a platinum

counterelectrode, and a reference electrode. The working electrode is polarized inside the selected electrolyte and the solution containing liquid fuel. It acts as the monitor of the potential of the working electrode to a reference electrode.

Drawing 3 shows polarization over a polarization curve, i.e., the current density expressed with milliamperes every square centimeter (mA/cm²), about the behavior of methanol oxidation in Nafion (trademark) and the electrolyte of a sulfuric acid. Here, a curve 41 shows polarization about the sulfuric acid electrolyte of 0.5M, and a curve 43 shows polarization about the Nafion (trademark) electrolyte. Polarization is expressed with the potential to NHE. NHE means a standard hydrogen electrode here.

These curves express the measurement data in 60 degrees C about the fuel which consists of underwater methanol mixed liquor of 1M. Polarization loss is smaller than the time of the direction when the electrode touches Nafion (trademark) touching the sulfuric acid so that drawing 3 may show. Therefore, the behavior of electric oxidation of a methanol can be concluded to be easy by the time of an electrolyte being Nafion (trademark). the fact that strong adsorption of sulfate ion takes place by the electrode / sulfuric-acid interface at the time of the electropositive potential to which these observation results bar the behavior of electric oxidation -- explanation attachment ****. Since such ion is not made when Nafion (trademark) is used as an electrolyte, such adsorption is not generated. Moreover, compared with the electrode / sulfuric-acid interface, it is believed that the behavior of electric reduction of oxygen or air is promoted in an electrode / Nafion (trademark) interface. Since the effectiveness of this latter has the more high fusibility of the oxygen to the inside of Nafion (trademark), it is thought that it will be because the anion to which it stuck strongly does not exist. Therefore, if the solid-state poly membrane of proton conductivity is used as an electrolyte, for the behavior of the reaction of both electrodes, it is advantageous and the fault of a sulfuric-acid electrolyte can be conquered.

Moreover, a sulfuric-acid electrolyte is disassembled at the temperature above 80 degrees C. The product by decomposition reduces the engine performance of each electrode. The electrochemical stability and thermal stability of a solid-state polyelectrolyte like Nafion (trademark) are fairly higher than that of a sulfuric acid, and the solid-state polyelectrolyte is usable at a no less than 120 degrees C elevated temperature. Therefore, if the solid-state poly membrane of proton conductivity is used, hot and prolonged fuel cell actuation like 120 degrees C will be attained, and the further advantage will be brought about. It is because the behavior of electric oxidation of a fuel and electric reduction of oxygen will happen easily all the time if temperature goes up.

Drawing 4 shows the case where the engine performance of the fuel cell shown in drawing 2 is operated at 65 degrees C about the combination of a methanol and oxygen, and the combination of a methanol and air. In drawing 4, the electrical potential difference of a fuel cell is expressed in accordance with a shaft 32, and current density is expressed with mA/cm² in accordance with the shaft 34. A curve 36 shows the engine performance of the combination of a methanol and oxygen, and a curve 38 shows the engine performance of the combination of a methanol and air. It presents that it is slightly better than air the engine performance [use / pure oxygen] so that it may understand here.

Drawing 5 shows the effectiveness of fuel concentration over the engine performance of a cell. The potential of a fuel cell is shown in accordance with a shaft 40, and current density is shown by mA/cm² in accordance with the shaft 42. A curve 44 shows the engine performance at the time of 150 Fahrenheit about 2.0-mol methanol solution. A curve 46 shows the engine performance at the time of 140 Fahrenheit about 0.5-mol methanol mixed liquor. A curve 48 shows the engine performance at the time of 160 Fahrenheit about the methanol mixed liquor of 4.0M. 2.0M methanol mixed liquor offers the best overall characteristic so that it may understand from now on. Moreover, drawing 5 shows that the high current density of 300 mA/cm² is maintainable, while a fuel cell maintains a high electrical potential difference rationally. Especially 2.0-mol methanol mixed liquor offers the electrical potential difference which exceeds 0.4 volts by about 300 mA/cm². The engine performance shown in drawing 5 expresses the significant improvement exceeding the engine performance of a former organic fuel cell. The anode of a fuel cell and the polarization operation of a cathode are shown as a function of the current density which took the electrical potential difference to drawing 6 in accordance with the shaft 50, took current density to it in accordance with the shaft 52, and was expressed with mA/cm² to it. A

curve 54 shows the polarization operation at the time of 150 Fahrenheit about 2.0-mol mixed liquor. A curve 56 shows the polarization operation about a fuel, and a curve 58 shows the polarization operation about oxygen.

The anode structure for a liquid supply mold fuel cell The anode structure for a liquid supply fuel cell must completely differ from it of the conventional fuel cell. The electrode structure of a gaseous diffusion mold which can bring about the balance of gas, a liquid, and a solid-state is used for the conventional fuel cell. However, the anode structure similar to a dc-battery is required for the fuel cell of a liquid supply mold.

The anode structure must be porosity and must be able to wet liquid fuel. In addition, the structure must have both [conductive] electronic conductivity and ion, in order to carry effectively an anode current collector (carbon paper), and hydrogen/hydronium ion for an electron to the Nafion (trademark) electrolyte membrane. Furthermore, the anode structure must be assistance to secure the convenient gas-evolution property in an anode.

An electrode required for the fuel cell of a liquid supply mold can also be made from special edition, or can also change the available conventional gas diffusion electrode with a suitable additive commercially.

Sinking [of the electrode in an ionomer additive] in An electrode catalyst bed and the anode base material 14 (drawing 1) made from a carbon fiber are good to sink in preferably with the proton electric conduction polymer additives of a hydrophilic property like Nafion (trademark). An additive is partially prepared in the interior of an anode so that the hydronium made from a proton and electric oxidation reaction can be carried effectively. Promoting also carried out soaking the pore of an electrode in homogeneity with the solution of the fuel/water of a liquid, and the ionomer additive has also realized better use of an electrode catalyst. The behavior of electric oxidation of the methanol by adsorption of an anion decreasing is also improved. Furthermore, it is assistance [secure / the convenient gas-evolution property for an anode] by using an ionomer additive.

In order are effective and to make an anode additive there be, it is a hydrophilic property, and an additive is proton conductivity, it should be electrochemically stable and should not bar the behavior of oxidation of liquid fuel. Nafion (trademark) satisfies these criteria and is a desirable anode additive. There are montmorillonite clay, a zeolite, an alkoxy cellulose, cyclodextrin, and a phosphate water ** zirconium in other hydrophilic properties and proton conductivity additive which are expected to have the same effectiveness as Nafion (trademark).

Drawing 7 is the block diagram showing the step concerning infiltrating an ionomer additive like Nafion (trademark) in an anode. The carbon-electrode structure is prepared first. The electrode structure of available large surface area carbon may be used for the commercial target which adopted what applied the mixture of a large surface area electrode catalyst and a Teflon (trademark) binder to the Toray Industries (trademark) carbon fiber paper. The electrode of an electrode catalysis also uses TFE-30 (trademark) which is the emulsion of polytetrafluoroethylene, and they are a large surface area catalyst particle and the Toray Industries (trademark) paper (both E-Tek, Inc).

since -- being available -- you may prepare. Although these structures can be prepared with the ingredient of the above-mentioned partial element, they can also obtain the structure beforehand made from the dimension of arbitration from direct E-Tek.

It sinks in by dipping an electrode catalyst particle for 5 to 10 minutes with an ionomer additive [like Nafion (trademark)] whose electrode is into the solution (based on the moderate dilution by the methanol or isopropanol of a solution supplied by Aldrich Chemical Co. or Solution Technologies Inc.) which contains 0.5 - 5% of ionomer additive at step 302. Subsequently, an electrode is picked out from a solution at step 304, and it is under reduced pressure among air, it dries at the temperature of the range of 20-60 degrees C, and the residue of the higher alcohol relevant to the Nafion (trademark) solution is volatilized. The sinking-in steps 302-304 are repeated until a desired composite (it is in 2 - 10% of range of the weight of an electrode catalyst) is obtained. Restoration of 0.1 to 0.5 mg/cm² is model. If the additive of an electrode composite exceeds 10%, it can result in bringing about the increment in the internal resistance of a fuel cell, and adhesive aggravation of the solid-state polyelectrolyte film. If there

are few additives to a composite than 2%, the improved electrode engine performance cannot be obtained typically.

In order to form a sinking-in electrode from an electrode catalyst particle, an electrode catalyst particle is mixed in the solution of Nafion (trademark) diluted with isopropanol to 1%. Subsequently, he leaves the solvent for evaporating and it is made thick mixed liquor. Subsequently, the thick mixed liquor is applied on the Toray Industries (trademark) paper, and the film of an electrode catalyst is formed. What applied the mixed liquor of the large surface area particle of a gram to the Toray Industries (trademark) paper whole about 200 square meters is model. Here, although I want you to observe, the electrode catalyst bed which carried out in this way and was formed has only Nafion (trademark), and Teflon (trademark) does not have. Thus, the prepared electrode is under reduced pressure, subsequently is dried at 60 degrees C for 1 hour, the residue of higher alcohol is removed, and it can be used by the liquid fuel cell after that.

According to the technique mentioned above, the available large surface area platinum-tin electrode was commercially sunk in by Nafion (trademark). Drawing 8 is measured in the half cell similar to the cell of drawing 10 (following) which carried out the deer and contained the sulfuric-acid electrolyte, and is comparing the engine performance of a Nafion (trademark) sinking-in electrode with the electrode which does not sink in. Drawing 8 especially shows the polarization measurement when using a sulfuric-acid electrolyte (0.5 mols) in a liquid formaldehyde fuel (one mol). The current density expressed with mA/cm² is shown in accordance with a shaft 306, and the potential expressed with the bolt is shown in accordance with a shaft 308. A curve 310 is a galvanostatic polarization curve (galvanostatic polarization curve) about the platinum-tin electrode which does not contain Nafion (trademark). A curve 312 is a galvanostatic polarization curve about the platinum-tin electrode which has not sunk in by Nafion (trademark).

Drawing 8 shows that much bigger current density than what has the electrode with which the direction which has a Nafion (trademark) sinking-in electrode has not sunk in can be obtained. In fact, it happens whether oxidation of formaldehyde is merely slight in the thing of the electrode which has not sunk in. Addition of Nafion (trademark) brings about an improvement dramatic in this way. In addition, that there is no hysteresis in a galvanostatic polarization curve means that these coatings are stable. What has so far been explained above is the amelioration anode of the liquid supply fuel cell which sank in with the ionomer additive. How to make contain an ionomer additive in an anode and manufacture was also explained. The remaining part of a detailed description explains using a perfluoro-octane sulfonic acid as the additive in the electro-deposition bath used in order to manufacture an electrode, and a direct additive in a fuel.

Electrodeposition of the electrode which used the perfluoro-octane sulfonic-acid additive With reference to drawing 9 -11, how to manufacture the electrode for using it for an organic fuel cell is explained below at a detail. This approach is adopted as manufacturing the cathode for using it for an above-mentioned liquid organic fuel cell, and is very advantageous. However, the electrode prepared by the approach of drawing 9 -11 can also be used for various organic fuel cells as an alternative of an old thing.

First, many steps of the approach of manufacturing an anode are explained with reference to drawing 9. First, in step 200, the carbon-electrode structure is prepared by applying the mixture of a large surface area carbon particle and a Teflon (trademark) binder to the carbon paper of the fiber base. Preferably, a carbon particle has the surface area of a gram (m²/g) the whole 200 square meters. The substrate of a suitable carbon particle, Vulcan Thing ** called XC-72 is E-Tek. It is available from Inc. It is desirable to add a Teflon (trademark) binder so that it may become 15% of rate by weight. The carbon paper of the fiber base is the Toray Industries (trademark) paper preferably, and is E-Tek similarly. It is available from Incorporated. The carbon structure may be prepared from the aforementioned partial element ingredient. Or instead, it is direct E-Tek. The structure by which marketing was beforehand made from Inc. is available with the square which is 2 inch x2 inch.

In step 202, a hexachloroplatinic acid (IV) and a potassium pen TAKURORAKO ruthenium (III) are dissolved into a sulfuric acid, and an electro-deposition bath is prepared. Preferably, the metal ion

concentration obtained as a result has good within the limits of 0.01-0.05M. Moreover, the concentration of a sulfuric acid of 1M is good preferably.

The above composite is adopted in order to electrodeposit a platinum-ruthenium on the carbon-electrode structure. Another solution may be adopted instead. For example, although platinum-tin electrodeposition is acquired, a stannic-chloride constituent is dissolved into a sulfuric acid.

In order to mainly prevent hydrolysis of a solution, the salt of a metal ion is dissolved into a sulfuric acid. As for the solution obtained above since a ruthenium was electrodeposited, it is desirable to deaerate in order to avoid formation of a higher oxidation state. In step 204, the perfluoro-octane sulfonic acid (C-8 acid) of a high grade is added to a bath. C-8 acid is good preferably to add to the concentration of the range of a liter the whole 0.1-1.0g. C-8 acid is prepared in order to make it easy to wet a carbon particle completely. C-8 acid is inactive electrically, and does not stick especially to the metal part inside the structure. Therefore, C-8 acid is harmless for the continuing electrodeposited process. It turned out that addition of C-8 acid is useful to altitude. And it is the need in order to make an electrode electrodeposited well probably.

At step 206, the carbon-electrode structure made at step 200 is arranged in the electro-deposition bath made at step 204. A platinum electrode is also arranged in the bath. A substitute anode ingredient may be adopted for electrodeposition of other metal ions.

Subsequently, an electrical potential difference is impressed between the carbon-electrode structure and a platinum anode at step 208. An electrical potential difference is applied for 10 minutes from about 5 until electrodeposition of a platinum-ruthenium becomes the amount of loading of about 5 mg/cm² on a carbon electrode. Preferably, the electrical potential difference of -0.8V is about applied to the reference electrode of mercury sulfate.

After the metal of the amount of a request on a carbon electrode is electrodeposited, an electrode is taken out at step 210 and it washes by deionized water. the inside of the deionized water which circulates through an electrode preferably -- at least 3 times and each time -- it is good for 15 minutes to wash. The step of washing is prepared in order to mainly remove the chloride and sulfate ion which are absorbed from the front face of a carbon electrode. This washing step was very desirable, and in order to make the effective electrode used for an organic fuel cell, it turned out that it is probably indispensable. It turned out that the electrode obtained by the manufacture approach of step 206 has the particle of a very uniform "*****" form with most quantity of the fine structure. It turned out that mean particle diameter is in 0.1-micron order.

The setup of the electrodeposited equipment used for performing the approach of drawing 9 is shown in drawing 10.

Speaking concretely, drawing 10's showing the cell 212 of 3 electrode molds which come to contain the single carbon structure electrode 214, the platinum counterelectrode (that is, anode) 216 of a pair, and a reference electrode 218. All electrodes are arranged in the bath 220 formed with above-mentioned metal / C-8 acid solution. The electric contact pieces 222 and 224 are arranged on the internal side face of a cell 212 in the upper part of a bath 220. The magnetic stirrer 226 is arranged inside the bath 220, and makes circulation easy with stirring of a bath. In order that the circulating water jacket 228 may use it for adjusting the temperature in a cell, it is prepared in the surroundings of a cell 212. The platinum anode is arranged in the frit 230 of fine glass, and the glass frit is prepared in order to insulate an anode from a cathode so that the oxidation product of an anode may not be spread into a cathode.

A reference electrode 214 is a reference electrode of mercury/mercurous sulfate. The reference electrode is prepared in order to supervise and control the potential of the carbon-electrode structure 214. desirable electrostatic-potential-(potentiostatic) and ***** -- the control approach of both [-like (galvanostatic)] is adopted. The constituent of alloy electrodeposition is controlled choosing the presentation of a bath, and by performing electrode electrodeposition with the upper current density enough from the limiting current density for metal electrodeposition, although summarized above. When choosing a proper bath presentation, it is important to normalize about the electrochemical equivalent of the metal in a constituent.

It is used for the amount of the charge passed from an anode to a cathode being detected, and

supervising the daily dose of the electrodeposited ingredient during actuation. In this point, the amount of the charge used for hydrogen release reaction must be deducted from each measured value of all charges. Although exactly good electrodeposition is based on the amount of request loading of actuation conditions and a catalyst, typically, it is produced within the period for 5 to 10 minutes. Since an operation and actuation of such equipment are well known to this contractor, the supervisory equipment used for supervising and controlling the potential of an electrode is not shown in drawing 10.

Drawing 11 shows the engine performance of the model electrode electrodeposited within the cell for electrodeposition of drawing 7 using the approach of drawing 9. In drawing 11, in accordance with a shaft 240, it takes per bolt of ***** to NHE, and current density is taken in accordance with the shaft 242 in the unit of mA/cm².

A curve 246 shows a galvanostatic polarization curve about the platinum-ruthenium alloy electrode supported with the carbon for making it the amount of loading of 5 mg/cm² according to the above. A curve 246 shows electrostatic ***** about an electrode which has the amount of loading of 1 mg/cm². As for the electrode, in any case, it was adopted in the interior of the sulfuric-acid electrolyte in a half cell. The fuel cell contains the organic fuel which consists of an one mol methanol and a 0.5-mol sulfuric acid, and was operated at 60 degrees C. When the amount of loading is 5 mg/cm², the electrode is maintaining the current density which 100 mA/cm² followed by 0.45 volts to NHE.

The result shown in drawing 11 is the example of the setmaster of the engine performance which will be attained using the electrode manufactured according to the approach of drawing 9. The further improvement in the engine performance will be attained by proper optimization of electrodeposited conditions and an alloy presentation. Therefore, the specific conditions or the concentration which were mentioned above are not necessarily the optimal, and the best mode currently cut by current [for manufacturing an electrode] is expressed.

Perfluoro-octane sulfonic acid as fuel additive (C-8 acid) Use of C-8 acid as an additive which can be set among an electro-deposition bath was described above. It was decided that it is also advantageous to add as an additive in the fuel of the liquid supply mold fuel cell which used the sulfuric-acid electrolyte as for C-8 acid. Especially, it has molecular formula C₈F₁₇SO₃H, and it was found out that C-straight chain 8 acid of the concentration of 0.001-0.1M is the wetting agent which was excellent in the liquid supply mold fuel cell.

Drawing 12 shows the experimental result in comparison with the fuel cell with which this additive was lacked in use of C-8 acid as an additive. Especially drawing 12 is Teflon (trademark) in a sulfuric-acid electrolyte.

The experimental result of the half cell using the electrode of the platinum supported by the carbon of the covered large surface area and a platinum alloy is shown. This result was obtained using the cell shown in drawing 10, and the same half cell. Drawing 12 shows the potential to NHE in alignment with a vertical axis 400, and the current density in mA/cm² in alignment with a horizontal axis 402. Four curves are having no additive (curve 404) and a thing which shows polarization about the fuel containing the additive (curve 406) of 0.0001M, the additive (curve 408) of 0.0001M, and the additive (curve 412) of 0.01M.

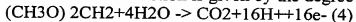
Addition of C-8 additive rather decreases polarization fairly so that drawing 12 may show. Although not illustrated, oxidation of a methanol was also completely investigated without the sulfuric acid using the pure C-8 acid solution of 0.1M. The polarization curve (illustration abbreviation) shows that reaction kinetics is not influenced by existence of perfluoro-octane sulfone ion.

Therefore, when the available fuel cell electrode by which Teflon (trademark) covering was carried out is commercially used for drawing 12, for the fuel cell which adopted the sulfuric acid as an electrolyte at least, the useful thing is proved [use / 0.001M or C-8 acid of the density range beyond it / as an additive] to a liquid fuel solution.

Three new fuels used for a liquid supply mold fuel cell are described about the remaining drawing. The fuel is dimethoxymethane, trimethoxy methane, and a trioxane.

Dimethoxymethane as a fuel for a liquid supply mold fuel cell Drawing 13 -15 show the result of the

experiment made as a fuel to an organic direct liquid supply mold fuel cell using dimethoxymethane (DMM). On the occasion of use, water was mixed even with the concentration of the range of Abbreviation 0.1-2M, and DMM was supplied to the fuel cell. Probably, other concentration will be effective. The fuel cell may include one or the amelioration beyond it which the thing of the usual design may be used for and was mentioned above. In a fuel cell, electric oxidation of the DMM is carried out with the anode of a cell. Electric oxidation of DMM includes the surface reaction which generates the carbon dioxide and water following a series of dissociation steps and it. This electrochemical reaction is given by the degree type.



The experiments which test electric oxidation of DMM are the cell equipped with the temperature control shown in drawing 10, and the same half cell, and were made using the sulfuric-acid electrolyte of 0.5M with the electrocatalysis electrode of Pt-Sn or Pt-Ru. The galvanostatic polarization curve shown in drawing 13 shows the electric oxidation property of DMM about the platinum-tin electrode in the fuel concentration from which some differ. This platinum-tin electrode is Etec of Massachusetts and the Framingham whereabouts, and Vulcan obtained from Inc. It is the thing of the gaseous diffusion type which consists of all metals of 0.5 mg/cm² supported on XC-72. In drawing 13, current density is shown in accordance with a shaft 500, and polarization (it saw with the potential to NHE) is given in accordance with the shaft 502. Curves 504, 506, 508, and 510 show polarization about 0.1M, 0.5M, 1M, and DMM of the concentration which becomes 2M, respectively. Drawing 13 shows that the behavior of oxidation of DMM is improved, if concentration increases. The curve of drawing 13 was measured with the half cell which adopted the sulfuric acid of 0.5M as an electrolyte with C-8 acid of 0.1M. This measurement was made at the room temperature.

DMM oxidizing with electronegative potential considerably and dealing in it rather than a methanol, was found out. Moreover, it was also found out that temperature affects the rate of oxidation considerably. However, DMM has the low boiling point of 41 degrees C. Therefore, for the attempt which it is going to use for a liquid supply mold fuel cell at temperature higher than this boiling point, difficulty produces DMM.

Drawing 14 shows polarization about two different concentration in two different temperature. Current density is given in accordance with a shaft 512, and polarization (it saw with the potential to NHE) is given in accordance with a shaft 514. A curve 516 shows polarization about DMM of the concentration of 1M in a room temperature. A curve 518 shows polarization about DMM of the concentration of 2M in 55 degrees C. Improved polarization will be attained, if higher concentration is used at higher temperature so that it may understand, if it sees. Moreover, the comparison with the curve 510 of drawing 13 and the curve 518 of drawing 14 shows that polarization by which increase of temperature has been improved about the same concentration level is produced. Therefore, it is sure of increase of temperature producing the result of the behavior of the improved electric oxidation.

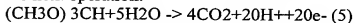
In addition to the experiment of the half cell shown in drawing 13 and 14, the experiment of a fuel cell was also made at the ** sake which verifies the effectiveness of DMM in a fuel cell. Direct oxidation of DMM in a fuel cell was performed by liquid supply mold fuel cell which was mentioned above by drawing 1 and 2.

Therefore, the solid-state poly membrane (Nafion 117 (trademark)) of proton conductivity was used for this fuel cell as an electrolyte. This membrane electrode assembly consists of a fuel oxidation electrode which consists of a catalyst bed (4 mg/cm²) of the platinum-ruthenium which is not supported, and a platinum electrode with which a gaseous diffusion type is not supported in order to decrease oxygen. This fuel cell used the solution of 1M of DMM for the fuel oxidation side, and used the oxygen of 20psi (s) for the cathode side.

Analysis of the oxidation product of DMM shows only the methanol. It is considered that a methanol is the intermediate product in the oxidation to which DMM becomes a carbon dioxide and water which may exist. However, a methanol and coexistence are possible for a fuel cell system, and since a methanol finally also oxidizes in a carbon dioxide and water, existence of the methanol as an intermediate product is not concerns.

The current-voltage characteristic of the liquid supply mold direct oxidation fuel cell which uses DMM as a fuel is shown in [drawing 15](#). This fuel cell operated at 37 degrees C. In [drawing 15](#), the current density in mA/cm² is given in accordance with the shaft 520. The cell voltage in a bolt is given in accordance with the shaft 522. The curve 524 shows cell voltage as a function of current density about the DMM solution of 1M mentioned above. As [drawing 15](#) shows, 50mA /of cell voltage in DMM reaches 0.25V by 2 cm, and this is height comparable as that (illustration abbreviation) which was attained with the methanol. It is higher temperature and the still better engine performance will be attained by making it operate using a Pt-Sn catalyst. The low boiling point of DMM also becomes a candidate to gas supply type actuation.

Therefore, it was found out from measurement of a half cell and all cells that DMM can be oxidized at a very high rate. Therefore, although DMM is the fuel excellent in use with a direct oxidation type fuel cell, it is sure of it. Moreover, DMM is avirulent, is the liquid of low vapor pressure and permits easy handling. In addition, DMM is compoundable from natural gas (methane) with the usual technique. Trimethoxy methane as a fuel for a liquid supply mold fuel cell [Drawing 16](#) -18 show the result of the experiment made as a fuel to an organic direct liquid supply mold fuel cell using trimethoxy methane (TMM). As mentioned above about DMM, on the occasion of use, water was mixed even with the concentration of the range of Abbreviation 0.1-2M, and TMM was supplied to the fuel cell. Probably, other concentration will be effective. The fuel cell may include one or the amelioration beyond it which the thing of the usual design may be used for and was mentioned above. In a fuel cell, electric oxidation of the TMM is carried out with the anode of a cell. The electrochemical oxidation of TMM is shown by the next operation.



The experiments which verify electric oxidation of TMM are the cell equipped with the temperature control shown in [drawing 10](#), and the same half cell, and were made using the Pt-Sn electrode with the sulfuric-acid electrolyte of 0.5M containing C-8 acid of 0.01M. The experimental result of these half cells is shown in [drawing 16](#) and 17.

[Drawing 16](#) gives the galvanostatic polarization curve about TMM of the concentration from which some of Pt-Sn electrodes mentioned above differ. This Pt-Sn electrode is Vulcan which is a gaseous diffusion type thing and is obtained from Etec of Massachusetts and the Framingham whereabouts, and Inc. It consists of all metals of 0.5 mg/cm² supported on XC-72. In [drawing 16](#), the current density in mA/cm² is given in accordance with a shaft 600, and polarization (it saw with the potential to NHE) is given in accordance with the shaft 602. Curves 604, 606, 608, and 610 show polarization about 0.1M, 0.5M, 1M, and TMM of the concentration which becomes 2M, respectively. [Drawing 16](#) shows that polarization improved in higher concentration level is attained. All the measurement results shown in [drawing 16](#) were obtained at the room temperature.

TMM oxidizing with electronegative potential considerably and dealing in it rather than a methanol, was found out. Moreover, it was also found out that temperature affects the oxidation rate of TMM. [Drawing 17](#) shows polarization in two different temperature by two different concentration. In [drawing 17](#), the current density in mA/cm² is given in accordance with a shaft 612 (it saw with the potential to NHE), Polarization is given in accordance with a shaft 614. A curve 616 shows polarization about the TMM concentration of 1M in a room temperature, and, on the other hand, a curve 618 shows polarization about TMM of the concentration of 2M in 55 degrees C. The curve of [drawing 17](#) was obtained using the Pt-Sn electrode in the sulfuric-acid electrolyte of 0.5M containing C-8 acid of 0.01M. Improved polarization will be attained, if higher concentration is used at higher temperature so that it may understand, if it sees. The comparison with the curve 618 of [drawing 17](#) and the curve 610 of [drawing 16](#) shows that polarization by which increase of temperature has been improved about the same concentration level is produced. Although not illustrated, at the temperature of 60 degrees C, it was found out that it is twice [at the time of 25 degrees C] the rate of oxidation of TMM of this. In addition to the experiment of the half cell shown in [drawing 16](#) and 17, the experiment of a total fuel cell was also made at the ** sake which verifies the effectiveness of TMM in a fuel cell. Direct oxidation of TMM in a fuel cell was performed by the liquid supply mold fuel cell of the type mentioned

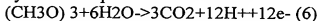
above by drawing 1 and 2. Therefore, the solid-state poly membrane (Nafion 117 (trademark)) of proton conductivity was used for this fuel cell as an electrolyte. The membrane electrode assembly of this fuel cell contains the catalyst bed (4 mg/cm²) of the platinum-ruthenium which is not supported, and the platinum electrode with which a gaseous diffusion type is not supported in order to decrease oxygen. This fuel cell used the solution of 2M of TMM for the fuel oxidation side, and used the oxygen of 20psi (s) for the cathode side.

The same with being related with DMM, analysis of the oxidation product of TMM shows only the methanol and it is considered that a methanol is the intermediate product in the oxidation from which TMM becomes a carbon dioxide and water which may exist. Since a methanol finally oxidizes in a carbon dioxide and water, for the fuel cell in which a methanol and coexistence are possible, existence of the methanol as an intermediate product is not concerns.

The current-voltage characteristic of the liquid supply mold direct oxidation fuel cell mentioned above is shown in drawing 18 about both TMM and a methanol. The current density in mA/cm² is given in accordance with a shaft 620, and cell voltage is given in accordance with the shaft 622. The curve 624 shows cell voltage as a function of current density about TMM of the concentration of 1M. The curve 626 shows the same thing about the methanol of the concentration of 1M. The measurement shown in drawing 18 was obtained at 65 degrees C. Although not illustrated, at TMM, cell voltage amounts to 0.52V by 300 mA/cm² at 90 degrees C, and this is a high value rather than it is obtained with a methanol.

Therefore, it was found out like DMM from measurement of a half cell and all cells that TMM can be oxidized at a very high rate. Moreover, like DMM, it is avirulent, and TMM is the liquid of low vapor pressure, it permits easy handling and can compound it from natural gas (methane) by the usual approach.

Trioxane as a fuel for a liquid supply mold fuel cell Drawing 19 -21 show the result of the experiment made as a fuel to an organic direct liquid supply mold fuel cell using the trioxane. As mentioned above about DMM and TMM, on the occasion of use, water was mixed even with the concentration of the range of Abbreviation 0.1-2M, and the trioxane was supplied to the fuel cell. Probably, other concentration will be effective. The fuel cell may include one or the amelioration beyond it which the thing of the usual design may be used for and was mentioned above. In a fuel cell, electric oxidation of the trioxane is carried out with the anode of a cell. The electrochemical oxidation of a trioxane is shown by the next operation.



The experiments which verify electric oxidation of a trioxane are the cell equipped with the temperature control shown in drawing 10, and the same half cell, and were made using the Pt-Sn electrode with 0.5M-2, and the sulfuric-acid electrolyte of 0M containing C-8 acid of 0.01M. The experimental result of these half cells is shown in drawing 19 and 20.

Drawing 19 gives the galvanostatic polarization curve about the trioxane of the concentration from which some of Pt-Sn electrodes mentioned above differ. This Pt-Sn electrode is Vulcan which is a gaseous diffusion type thing and is obtained from Etec of Massachusetts and the Framingham whereabouts, and Inc. It consists of all noble metals of 0.5 mg/cm² supported on XC-72. In drawing 19, the current density in mA/cm² is given in accordance with a shaft 700, and polarization (it saw with the potential to NHE) is given in accordance with the shaft 702. Curves 704, 706, 708, and 710 show 0.1M, 0.5M, 1M, and polarization about the trioxane of concentration that becomes 2M, respectively. Drawing 19 shows that polarization improved in higher concentration level is attained. All the measurement results shown in drawing 19 were obtained at 55 degrees C.

Therefore, about a trioxane, the increasing fuel concentration produces the result of increase of an oxidation rate. Moreover, the current density which reaches 100 mA/cm² is obtained in potential called 0.4V to NHE so that drawing 19 may show. This engine performance is equal to the engine performance attained with formaldehyde. Although not illustrated, research of cyclic voltammetry decided that the mechanism of oxidization of a trioxane did not include the decomposition to the formaldehyde before electric oxidization.

Moreover, increase of electrolytic acid concentration and producing the result of increase of an electric oxidation rate were also found out. Drawing 20 shows polarization in four different electrolytic concentration and two different temperature. In drawing 20, the current density in mA/cm² is given in accordance with a shaft 712, and polarization (with potential to NHE) is given in accordance with the shaft 714. The curve 716 shows polarization about the electrolytic concentration of 0.5M in a room temperature. The curve 720 shows polarization about the electrolytic concentration of 1M in 65 degrees C. The curve 722 shows polarization about the electrolytic concentration of 2M in 65 degrees C to the last. About all of curves 716-722, the concentration of a trioxane was 2M.

The curve of drawing 20 was obtained using the Pt-Sn electrode in the sulfuric-acid electrolyte containing C-8 acid of 0.01M. Improved polarization will be attained, if higher concentration is used at higher temperature so that it may understand, if it sees. Therefore, since Nafion (trademark) showed acidity equivalent to the sulfuric acid of 10M, when using Nafion (trademark) as an electrolyte, it was expected that an electric, very high oxidation rate is expectable.

In addition to the experiment of the half cell shown in drawing 19 and 20, the experiment of a total fuel cell was also made at the ** sake which verifies the effectiveness of the trioxane in a fuel cell. Direct oxidation of the trioxane in a fuel cell was performed by the liquid supply mold fuel cell of the type mentioned above by drawing 1 and 2. Therefore, the solid-state poly membrane (Nafion 117 (trademark)) of proton conductivity was used for this fuel cell as an electrolyte. This fuel cell used the solution of 1M of a trioxane for the fuel oxidation side, and used the oxygen of 20psi(s) for the cathode side.

The same with being related with DMM and TMM, analysis of the oxidation product of a trioxane shows only the methanol and it is considered that a methanol is the intermediate product in the oxidation from which TMM becomes a carbon dioxide and water which may exist. Since a methanol finally oxidizes in a carbon dioxide and water, for the fuel cell in which a methanol and coexistence are possible, existence of the methanol as an intermediate product is not concerns.

The current-voltage characteristic of the liquid supply mold direct oxidation fuel cell mentioned above is shown in drawing 21 about the trioxane. The current density in mA/cm² is given in accordance with a shaft 724, and cell voltage is given in accordance with the shaft 726. The curve 728 shows cell voltage as a function of current density about the trioxane of the concentration of 1M. The measurement shown in drawing 21 was obtained at 60 degrees C. The engine performance shown in drawing 21 will improve considerably by using a platinum-tin electrode rather than a Pt-Ru electrode.

Measurement (measurement of crossover) (illustration abbreviation) of the migration in a trioxane / oxygen fuel cell suggests that passing speed (rate of crossover) is at least 5 times as low as the thing in a methanol fuel cell. Since migration affects the effectiveness and the engine performance of a fuel cell as mentioned above, the passing speed which decreased is very desirable.

Therefore, it was found out like DMM and TMM from measurement of a half cell and all cells that a trioxane can be oxidized at a very high rate.

Conclusion The various amelioration to the liquid supply mold fuel cell which includes the set of three new fuels in the additive list for improving an approach having been improved for assembling the improved electrolyte and electrode structure, and an electrode and the fuel engine performance was explained. These various amelioration may be carried out separately, and most may be together put in order to attain the still higher engine performance. However, it is expected that it is effective to use C-8 acid as an additive to the fuel mentioned above only about the fuel cell which adopted an acid electrolyte like a sulfuric acid, and if adopted using the fuel cell which consisted of proton exchange film, it should care about that it may not be effective.

The approach, example, and experimental result which were indicated here are mere illustration and explanation of this invention, and should not be interpreted as what limits the range of this invention.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

1. In liquid supply mold direct fuel cell which comes to have means to circulate oxygen through means and cathode which are made to circulate through organic fuel through anode, cathode, electrolyte, and anode The solid-state polyelectrolyte film is adopted as an electrolyte. Amelioration which comes to contain supplying the organic fuel which does not have an acid electrolyte substantially.
2. It is amelioration according to claim 1. That said whose film is solid-state proton exchange film.
3. It is amelioration according to claim 2. That said film is made of Nafion (trademark).
4. It is amelioration according to claim 2. What is made of the pel full ORINETO sulfonic-acid polymer which said film changed.
5. It is amelioration according to claim 2. That said film is made of the poly hydrocarbon sulfonic-acid polymer.
6. It is amelioration according to claim 2. That said film is made of the composite of two or more proton exchange film.
7. It is amelioration according to claim 1. What is chosen from the group which said organic fuel becomes from a methanol, formaldehyde, and a formic acid.
8. It is amelioration according to claim 1. What is chosen from the group which said organic fuel becomes from dimethoxymethane, trimethoxy methane, and a trioxane.
9. It is amelioration according to claim 1. Thing to which said anode makes the ionomer of water-insoluble nature come to sink into a commercial electrode by the proton conductivity of a hydrophilic property.
10. It is amelioration according to claim 9. That said whose ionomer is Nafion (trademark).
11. It is amelioration according to claim 9. That said whose ionomer is montmorillonite clay.
12. It is amelioration according to claim 9. That said whose ionomer is an alkoxy cellulose.
13. It is amelioration according to claim 9. That said whose ionomer is cyclodextrin.
14. It is amelioration according to claim 9. That said whose ionomer is the mixture of a zeolite.
15. It is a fuel cell according to claim 9. That said whose ionomer is a phosphate water ** zirconium.
16. Anode Cathode Said anode and solid-state polyelectrolyte film prepared between said cathodes It is the means which is that in which the solution of a liquid organic fuel and water is circulated through said anode, and the solution concerned does not contain the sulfuric acid substantially. Liquid supply mold fuel cell which comes to have a means to circulate oxygen through said cathode.
17. Anode into which the ionomer of the water-insoluble nature of proton conductivity of a hydrophilic property was infiltrated Cathode Said anode and polyelectrolyte film prepared between said cathodes A means to circulate the solution of a liquid organic fuel and water through said anode Liquid supply fuel cell which comes to have a means to circulate oxygen through said cathode.
18. It is a fuel cell according to claim 17. That said whose film is solid-state proton exchange film.
19. It is a fuel cell according to claim 18. That said film is made of Nafion (trademark).
20. It is a fuel cell according to claim 18. What is made of the pel full ORINETO sulfonic-acid polymer which said film changed.

21. It is a fuel cell according to claim 18. That said film is made of the poly hydrocarbon sulfonic-acid polymer.
22. It is a fuel cell according to claim 18. That said film is made of the composite of two or more proton exchange film.
23. It is a fuel cell according to claim 17. What is chosen from the group which said organic fuel becomes from a methanol, formaldehyde, and a formic acid.
24. It is a fuel cell according to claim 17. What is chosen from the group which said organic fuel becomes from dimethoxymethane, trimethoxy methane, and a trioxane.
25. It is a fuel cell according to claim 17. That said whose ionomer is Nafion (trademark).
26. It is a fuel cell according to claim 17. That said whose ionomer is montmorillonite clay.
27. It is a fuel cell according to claim 17. That said whose ionomer is an alkoxy cellulose.
28. It is a fuel cell according to claim 17. That said whose ionomer is cyclodextrin.
29. It is a fuel cell according to claim 17. That said whose ionomer is the mixture of a zeolite.
30. It is a fuel cell according to claim 17. That said whose ionomer is a phosphate water ** zirconium.
31. Housing Which Has Anode Chamber and Cathode Chamber Nafion (Trademark) Polyelectrolyte Film Which is Attached in Said Housing and Separates Said Anode Chamber and Said Cathode Chamber Cathode Formed on 1 Side Face of Said Film Facing Cathode Chamber It is Formed on Opposite Side of Said Film Facing Anode Chamber, and is Nafion (Trademark).
- Infiltrated anode A means to circulate the solution of a liquid organic fuel and water through said anode A means to circulate oxygen through said cathode Means which samples a carbon dioxide from said anode chamber Liquid supply fuel cell which comes to have the means which samples oxygen and water from said cathode chamber.
32. The electrode which comes to have the metal alloy into which the ionomer of proton conductivity of the water-insoluble nature of a hydrophilic property was infiltrated.
33. It is the approach of processing the carbon structure made in the carbon particle of the large surface area supported with the binder. Step immersed into the bath containing a liquid pel full ORINETO sulfonic-acid polymer in the carbon structure How to come to contain the step which takes out said carbon structure and is dried.
34. It is an approach according to claim 33. That to which said polymer is characterized by being the solution of Nafion (trademark) 1% in a methanol.
35. It is an approach according to claim 33. What is characterized by performing from 5 the step immersed into the bath containing a liquid polymer in said carbon structure for 10 minutes.
36. The structure processed by the approach of claim 33.
37. In the electro-deposition bath used for manufacturing the electrode used for a liquid supply mold fuel cell Amelioration including adding the perfluoro-octane sulfonic acid of the amount in said bath.
38. It is Approach of Manufacturing Electrode Used for Fuel Cell. Step Which Offers Bath Which Contains Solution Which Dissolved Metal Salt in Sulfuric Acid, The step which adds a perfluoro-octane sulfonic acid to said bath, Step which arranges the large surface area carbon-electrode structure in said bath Step which arranges an anode in said bath How to come to contain the step which applies an electrical potential difference between said anodes and said electrodes until the metal of a desired amount accumulates on said electrode.
39. It is an approach according to claim 38. Approach characterized by said metal salt containing a hexachloroplatinic acid and a potassium pen TAKUROROAKO ruthenium.
40. It is an approach according to claim 38. Approach characterized by said anode being made of platinum.
41. It is an approach according to claim 38. Approach characterized by including the carbon which said carbon-electrode structure combined with the Teflon (trademark) binder.
42. It is an approach according to claim 38. Approach characterized by said carbon electrode containing the large surface area carbon which was combined with 15% of the weight of the Teflon (trademark) binder, and was applied on the fiber layer of a carbon pace.
43. It is an approach according to claim 38. Approach characterized by preparing said acid by the

concentration of the range of 0.01-0.05M.

44. It is an approach according to claim 38. Approach characterized by coming to contain the step which extracts said electrode from said bath and is further washed by deionized water.

45. It is Approach of Manufacturing Electrode Which Metal Ion for Using it for Liquid Organic Fuel Cell Deposited on it. The bath containing the solution of the hexachloroplatinic acid which dissolved into sulfuric acid, and a potassium pen TAKUROROAKO ruthenium is offered. The step which has the concentration of the range said hexachloroplatinic acid and whose potassium pen TAKUROROAKO ruthenium are 0.01-0.05M, The step which adds perfluoro-octane sulfonic acid to said bath by the concentration of the range of 0.1-1.0g/l., Arrange a large surface area carbon electrode in said bath, and said carbon-electrode structure has a carbon particle with a surface area of about 200m²/g and the mixture of a Teflon (trademark) binder. Step by which the mixture is applied to the carbon paper of the fiber base Step which arranges a platinum electrode in said bath Between said anodes and said electrodes How to come to contain the step which applies an electrical potential difference until the platinum and the ruthenium of the amount of requests deposit on said electrode.

46. The electrode manufactured by the approach according to claim 45.

47. In a liquid supply mold fuel cell Amelioration including adding the perfluoro-octane sulfonic acid of the amount in the fuel of a fuel cell.

48. It is amelioration according to claim 47. Amelioration characterized by preparing that said perfluoro-octane sulfonic acid is also at the concentration of at least 0 and 0.001M.

49. It is amelioration according to claim 48. Amelioration characterized by said perfluoro-octane sulfonic acid being in the range of 0.0001M to 0.01 mols.

50. Anode Cathode A means to circulate a liquid organic fuel, water, an acid electrolyte, and a perfluoro-octane sulfonic-acid addition solution through said anode Liquid supply mold fuel cell which comes to have a means to circulate oxygen through said cathode.

51. Anode Cathode Electrolyte A means to circulate the liquid organic fuel chosen from the group who consists of a trioxane, dimethoxymethane, and trimethoxy methane through said anode Liquid supply mold fuel cell which comes to have a means to circulate oxygen through said cathode.

52. It is a fuel cell according to claim 51. What is characterized by said fuel dissolving in the concentration between 0.1 and 2.0M into water.

53. It is the approach of generating energy. Step which offers a liquid supply mold fuel cell How to come to contain the step which operates said liquid supply mold fuel cell using the organic fuel chosen from the group who consists of a trioxane, dimethoxymethane, and trimethoxy methane.

[Translation done.]

図 1

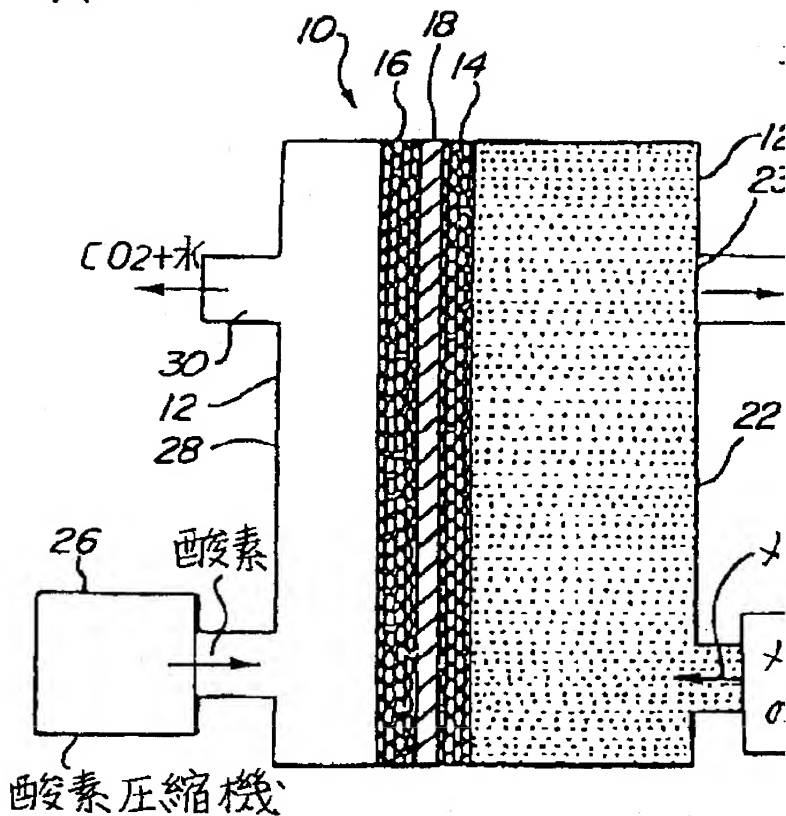
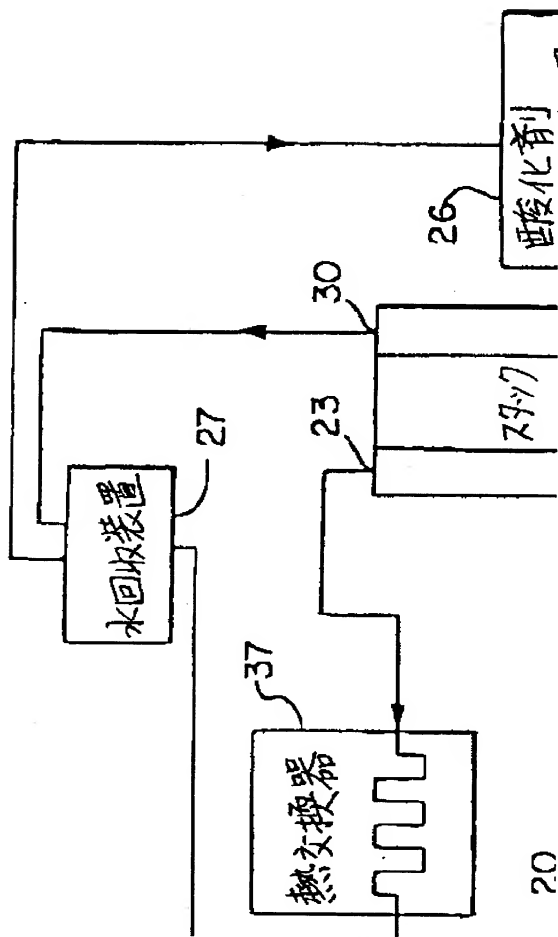


図 2



3

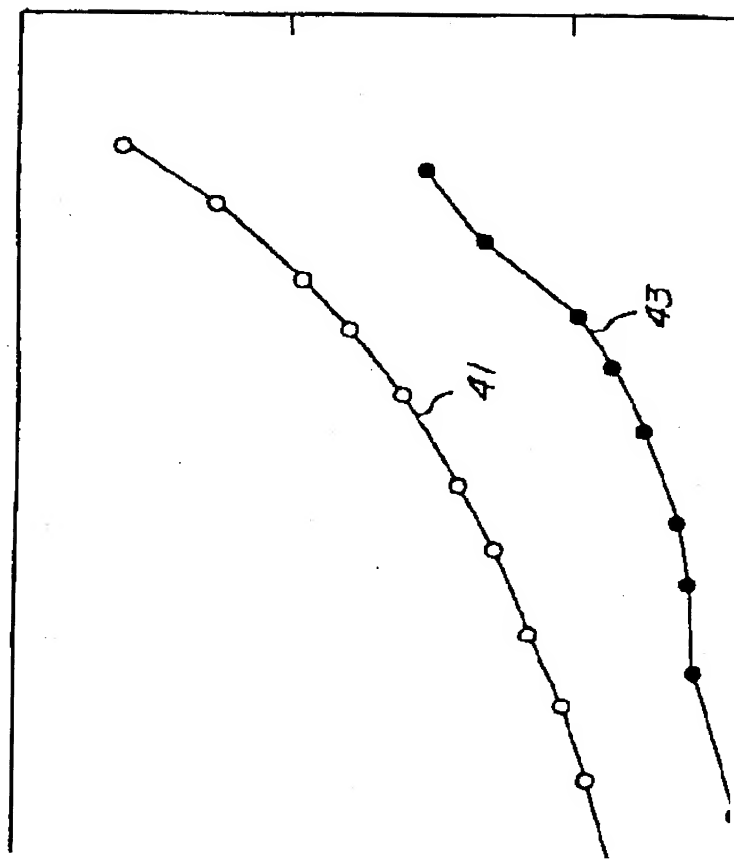
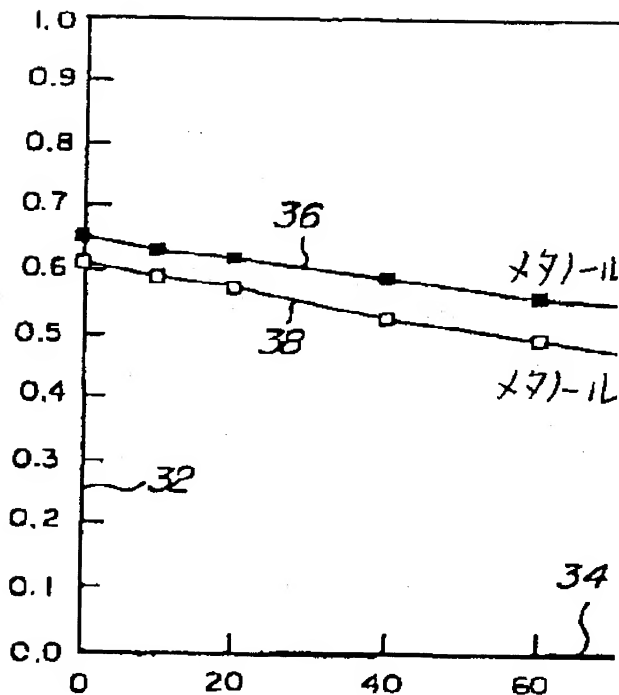


図 4

電圧
(ボルト)

電流密度 (mA)

図 5

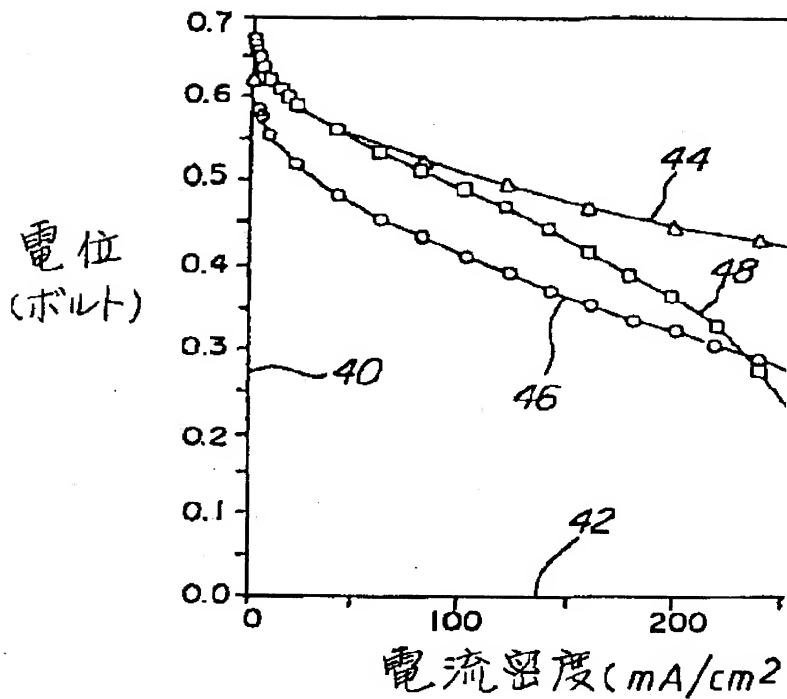


図 6

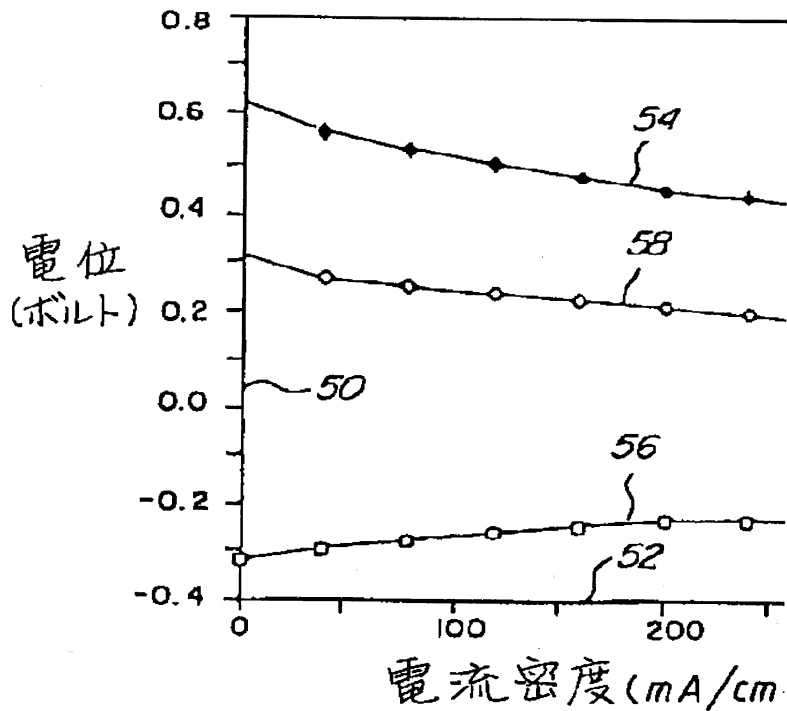
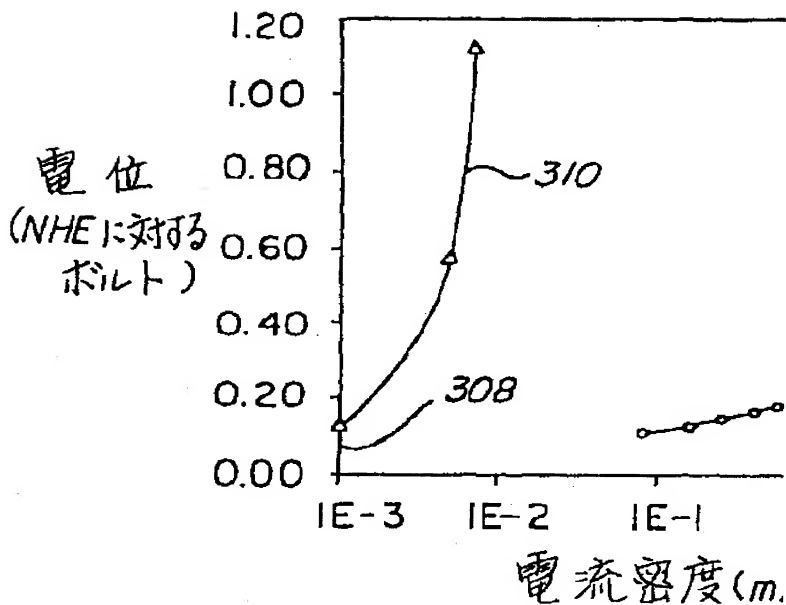


図 7

炭素電極構造体を、メタノール中ナフ
タレン溶液中に約5分間浸漬して、ナフ
タレン構造体の中へ $0.1 \sim 0.5 \text{ mg/cm}^2$ の装荷
させる。

電極を溶液から取り出して減圧中で

図 8



9

炭素繊維紙に、 $200\text{m}^2/\text{g}$ の大表面積
テフロン結合剤の混合物を塗布し
構造体を製造する。

$0.01\sim 0.05\text{M}$ の範囲の金属イオン
1M硫酸に溶解して、ヘキサクロロ
カリウムペンタクロロアコルテニウムの浴

ペルフルオロオクタンシルホン酸を
 $0.1\sim 1.0\text{g/l}$ の範囲の濃度にする。

トキシ性表面処理を、合金マシ、バ

10

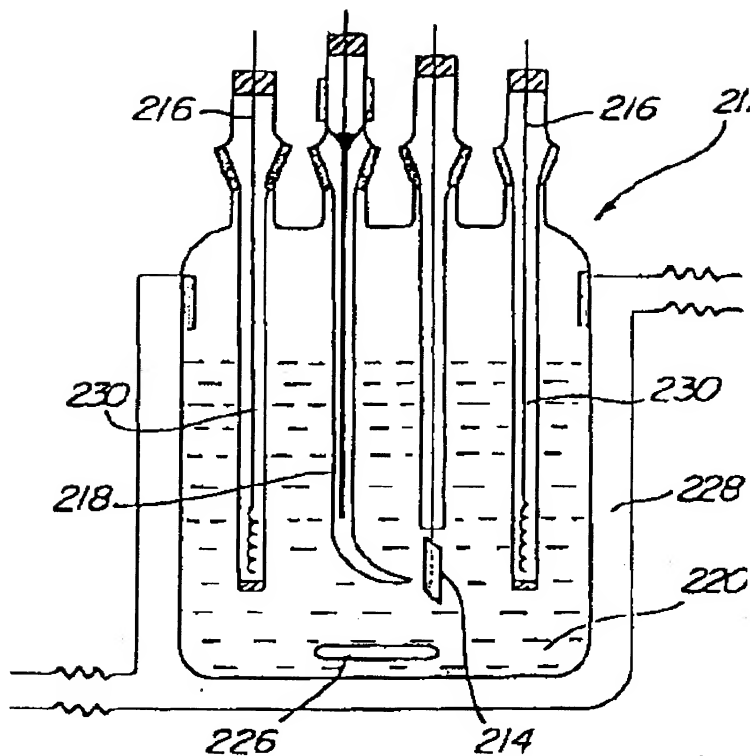


図 11

電位
(NHEに対する
ボルト)

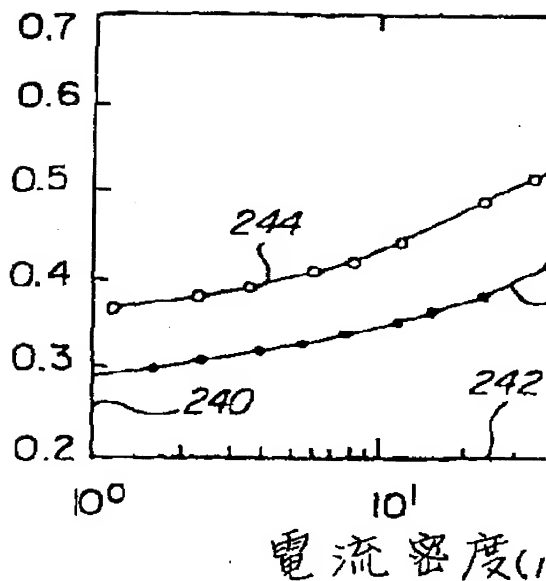


図 12

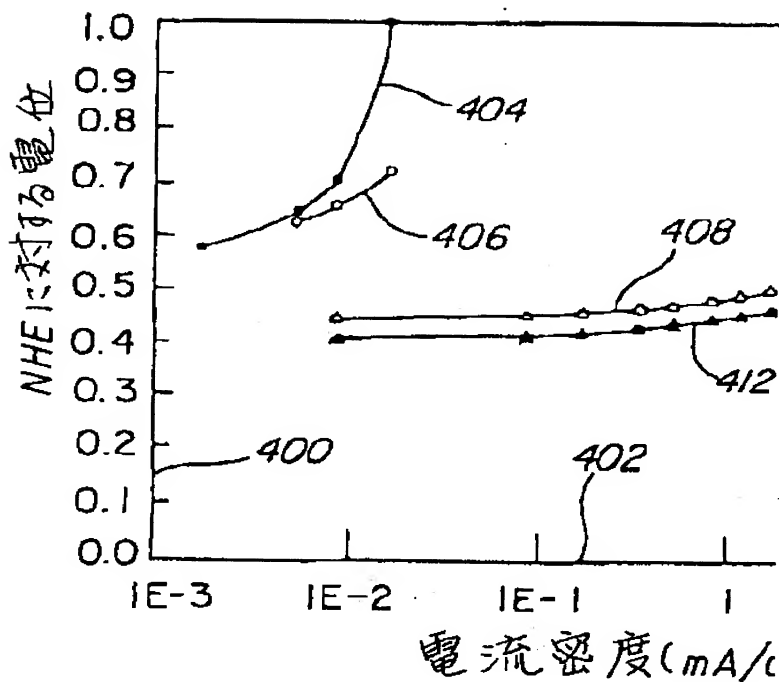


図 13

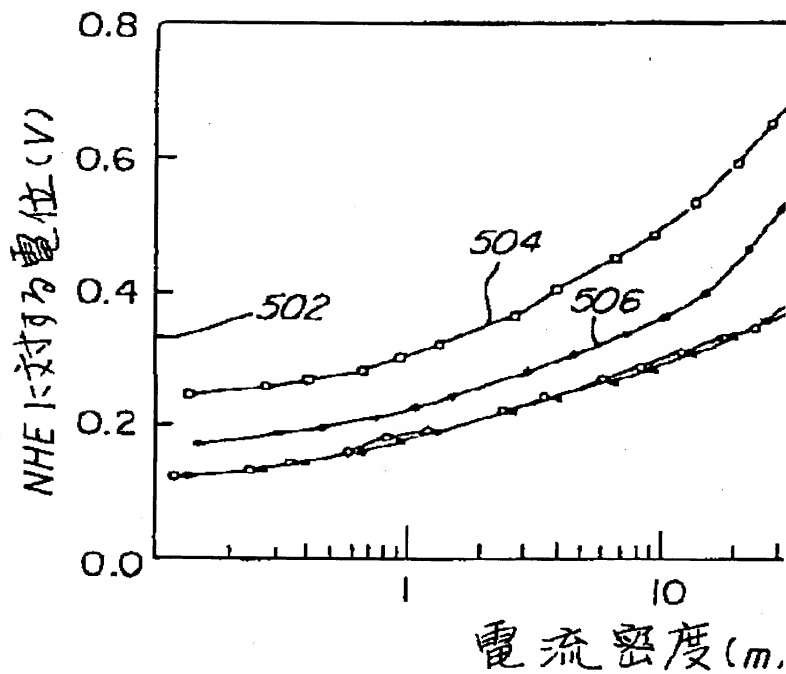


図 14

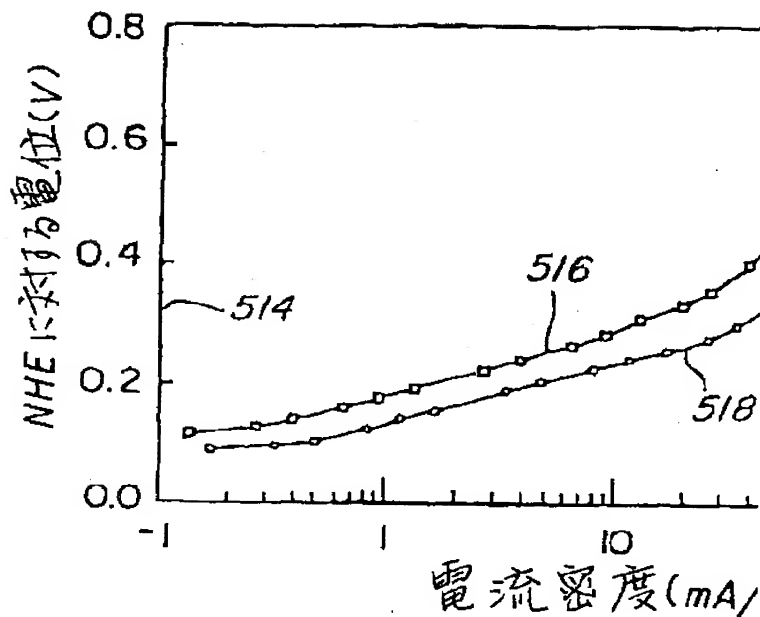


図 15

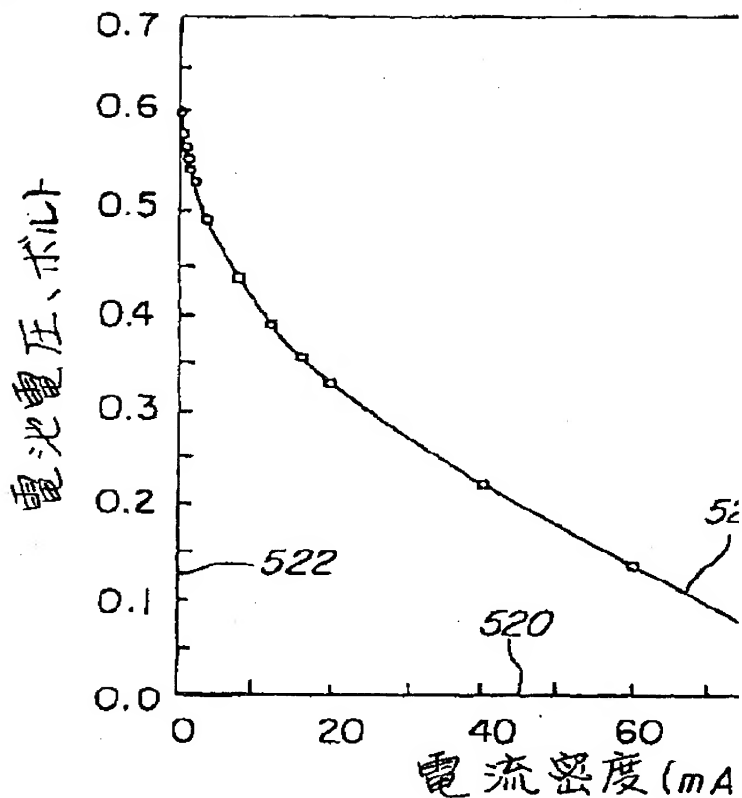


図 16

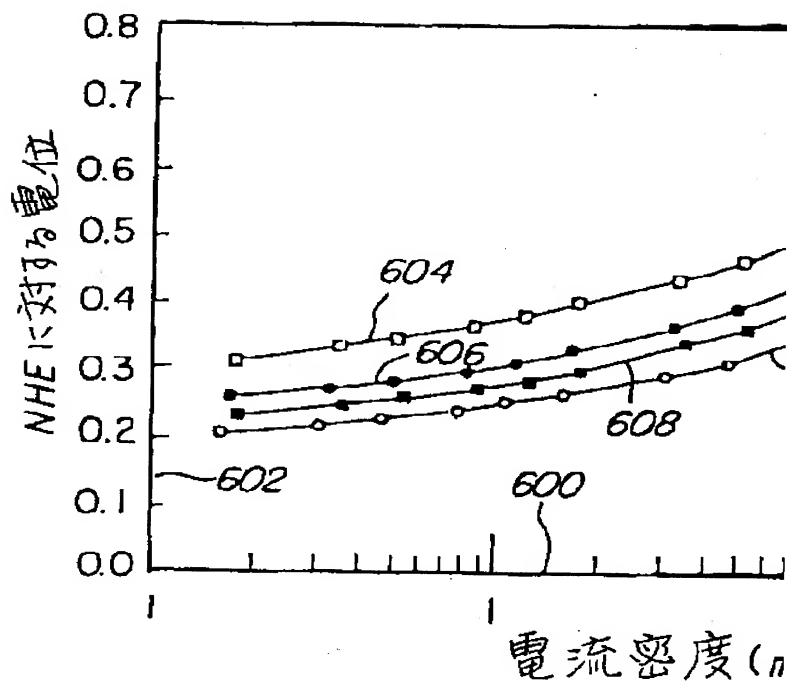


図 17

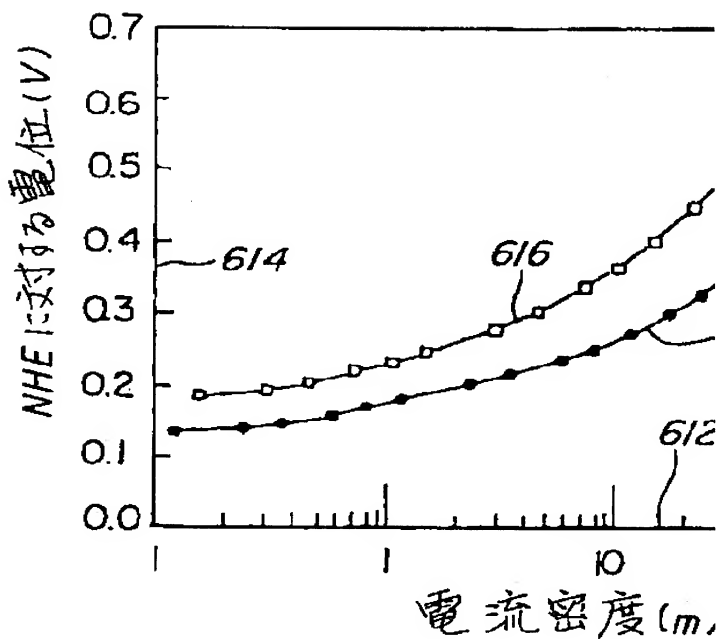


図 18

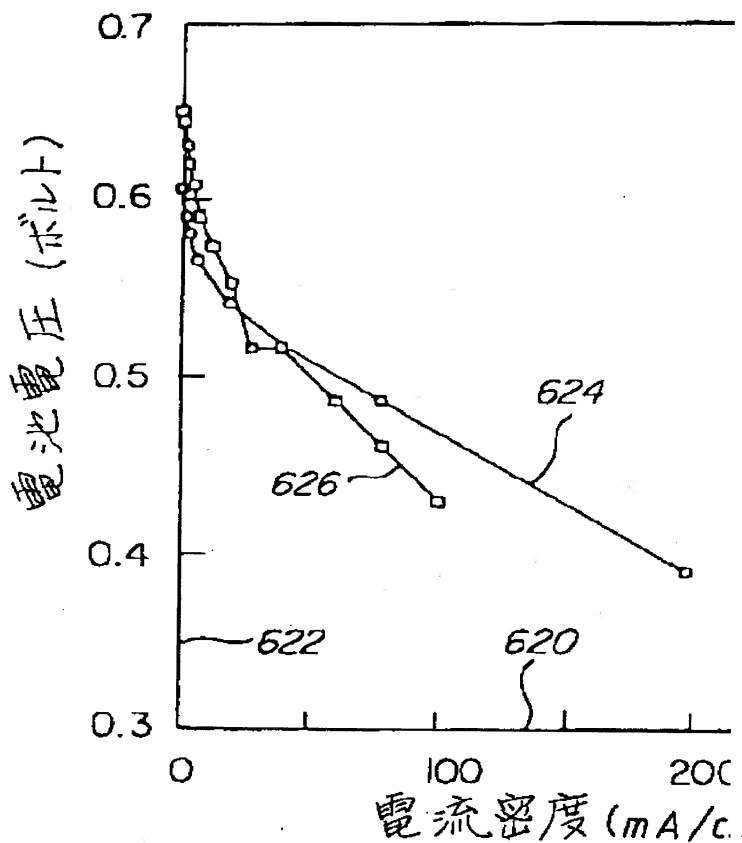


図 19

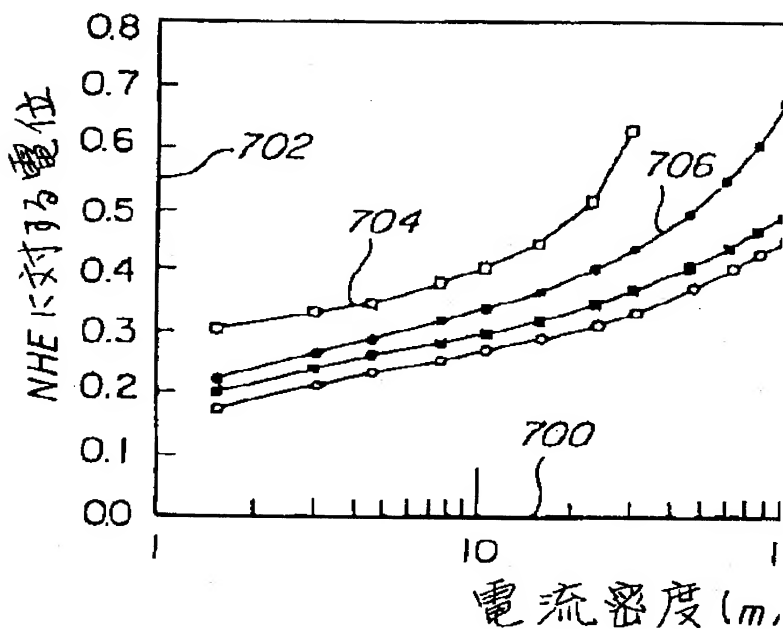


図 20

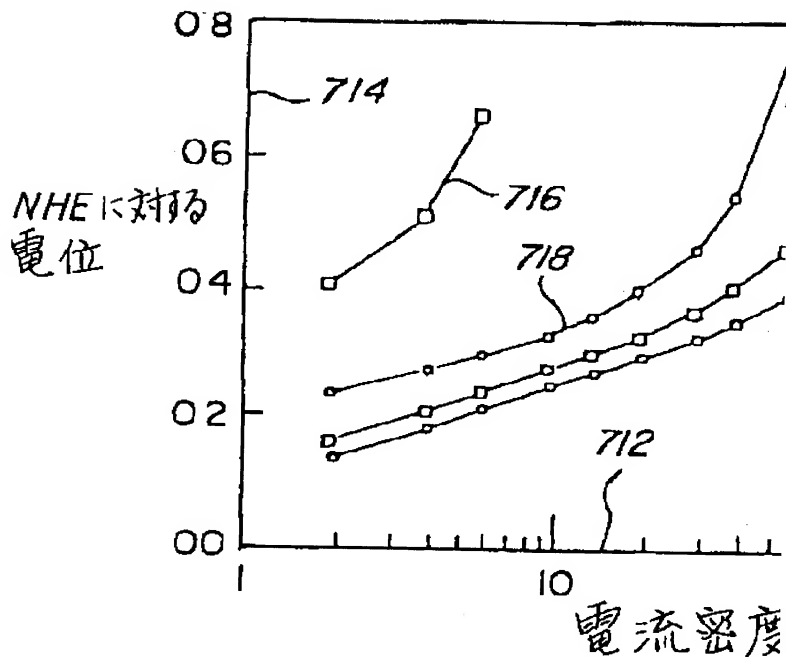


図 21

